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The theoretical analysis of experimental autoregrigeration kinetic data

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THE THEORETICAL ANALYSIS OF EXPERIMENTAL AUTOREGRIGERATION KINETIC DATA

by

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CERTIFICATE OF APPROVAL

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1. ABSTRACT

The aim of the present work was to conduct a theoretical analysis of the performance data of a small scale auto-refrigerated reactor to ascertain the mechanisms prevailing when autorefrigeration is employed. The reaction system under investigation involves catalyzed liquid phase reaction between ethylene and chlorine. The reactant gases are bubbled in the liquid product ethylene dichloride (EDC). An undesirable substitution reaction producing hydrogen chloride and trichloroethane also occurs.

The experimental data of Seaton are modified to account for the losses of EDC out of the condenser, which was located above the reactor. The relationship between autorefrigeration steady state temperature, conversion and yield of ethylene was established and was used to adjust the experimental data. The solubility of ethylene with or without catalyst was experimentally determined.

A liquid film diffusion model was proposed and examined in light of three possibilities for the substitution side reaction: (a) occurring in the bulk liquid phase; (b) occurring in the bulk vapor phase; and (c) occurring in the liquid film.

The liquid film reaction model with substitution reaction occurring in the bulk liquid phase gave a consistent explanation of the experimental observations.

II. INTRODUCTION

Autofrigeration is a popular method for removing exothermic heat of reactions. Important industrial applications include sulfuric acid alkylation of butylenes with isobutane to form high octane gasoline, halogenation of sodium-lead alloys to produce tetraethyl and tetramethyl lead, many halogenations, polymerisation of ethylene and chlorination of ethylene to make ethylene dichloride.

In conventionally cooled reactors heat is removed through cooling jackets, internal cooling coils or internal heat exchangers. Some problems associated with these systems are solid deposition on cooling surfaces, corrosion, erosion if suspended solid particles are present, imperfect mixing and resulting temperature gradients and leakage of reactor fluids.

In an autorefrigerated reactor, the exothermic heat of reaction is removed by vaporizing a liquid. The liquid could be a reactant, a product, a solvent or a combination of these. Besides offering freedom from the problems associated with conventional cooling, the advantages of autorefrigeration include improved mixing, improved heat transfer capacity, better temperature control and simplified equipment. Improved mixing causes more uniform temperature and concentration which is particularly important in polymeric and slurry reactions. Improved heat transfer capacity fascilitates

removal of large quantities of heat and more precise control of operating temperature. Weisser [1] reports that in polyethylene manufacture, the output of the same polymerisation reactor was tripled when conventional cooling was replaced by autorefrigeration. This improvement was attributed to improved heat transfer capacity. Elimination of the need of circulating pumps and external cooling coil results in simplified equipment which is easier to operate.

It is possible that autorefrigeration might have an adverse effect on a particular reaction system. In gas-sparged reactors, autorefrigeration might result into dilution of reactant gas feed due to vaporization and hence reduction in mass transfer driving force.

In an autorefrigeration reactor system, the steady state operating temperature is a function of the operating pressure for given compositions in the reactor. If temperature sensitive reactions and/or products are involved, the reactor must be operated at low pressures or an inert recycle must be used.

Some EDC product is lost in the exit gas stream from the condenser which consists of the unreacted reactant gases and the byproduct HCℓ. This EDC loss increases as the operating pressure decreases. A higher loss would occur in autorefrigeration where low pressures are used unless low temperature cooling is used in the condenser.

Gas-liquid reactions are an important part of the chemical industry. Much experimental and theoretical work has been accomplished in this field. Danckwerts [2] has given a thorough survey of literature on fundamentals, kinetics, mechanisms and design of the equipment involved in gas liquid contacting.

The fluid mechanics aspects of gas-sparged stirred tank reactors are well investigated. Danckwerts et al. [3,4,5,6] have investigated bubble size, mass transfer coefficients, interfacial area, bubble coalescence effect of surface active solutes in gas-sparged stirred reactor at great length. However, no one has so far reported the effect of evaporation on the kinetic aspects of gas-sparged stirred tank reactors.

With this background, George Seaton [7] conducted an experimental study of autorefrigeration.

He selected chlorine-ethylene-EDC reaction system for investigation and obtained performance data for a small scale reactor with two modes of heat removal at various temperatures, pressures, feed rates, catalyst concentrations and feed rates. He also suggested some probable mechanistic models which might explain the experimental data.

The purpose of the present work is to carry out further theoretical analysis of the experimental performance data and to ascertain the mechanisms prevailing when autorefrigeration is employed.

III. SUMMARY OF THE PREVIOUS WORK

1. Introduction

George Seaton decided to study the reaction system involving liquid phase reaction between chlorine and ethylene in the product ethylene dichloride (liq) because autorefrigeration had been profitably applied to this system in industry and because a study of conventionally cooled reaction had been reported by Balasubramaniam et al. [8]. They suggested a diffusion controlled liquid film model.

EDC is produced by chlorination of ethylene:

$$C_2H_{4(g)} + Cl_{2(g)} \rightarrow C_2H_4Cl_2(\ell) \ .$$

This reaction is exothermic, liberating about 52 kcal/gm-mole of ethylene reacted.

This reaction system has a tendency to form higher chlorinated byproducts mainly ethylene trichloride (ETC). ETC could be formed by the substitution reaction:

$$C_2H_4Cl_{2(\ell)} + Cl_{2(g)} \rightarrow C_2H_3Cl_{3(\ell)} + HCl_{(g)} \ .$$

This reaction is exothermic liberating 24 kcal/gm mole of chlorine reacted.

ETC might be formed by direct action of chlorine on ethylene:

$$C_2H_{4(g)} + 2Cl_{2(g)} \rightarrow C_2H_3Cl_{3(\ell)} + HCl_{(g)} \ .$$

In industry, the catalysts ferric chloride and antimony chloride, which are dissolved in the liquid product, have been found mandatory to attain adequate reaction rate and to suppress the undesirable side reactions.

2. Apparatus

Figure 1 depicts the experimental setup used by Seaton. The reactor was a cylindrical glass vessel with hemispherical bottom. The inside diameter was 10.8 cm. The net free cross-sectional area was 90 cm^2, with baffles, agitators and feed tube in place. The total reactor capacity was 2000 cc. Vertical baffles were inserted to prevent vortexing. The agitator was an 8-blade, 3.81 cm-diameter turbine, driven by an air motor.

The reactor was provided with a jacket through which cold water could be circulated. The reactor was well insulated for adiabatic operation.

The flow rates of reactant gases from cylinders were controlled by flow meters with needle valves on the down-stream side. Interchangeable meter tubes permitted flow rates of 0 - 2200 cc pm (@ 2.5°C, 1 atm).

The glass, spiral coil condenser (400 mm length) was such that reflux could be returned in toto to the reactor (batch operation) or a portion of it removed during the continuous autorefrigerated operation.

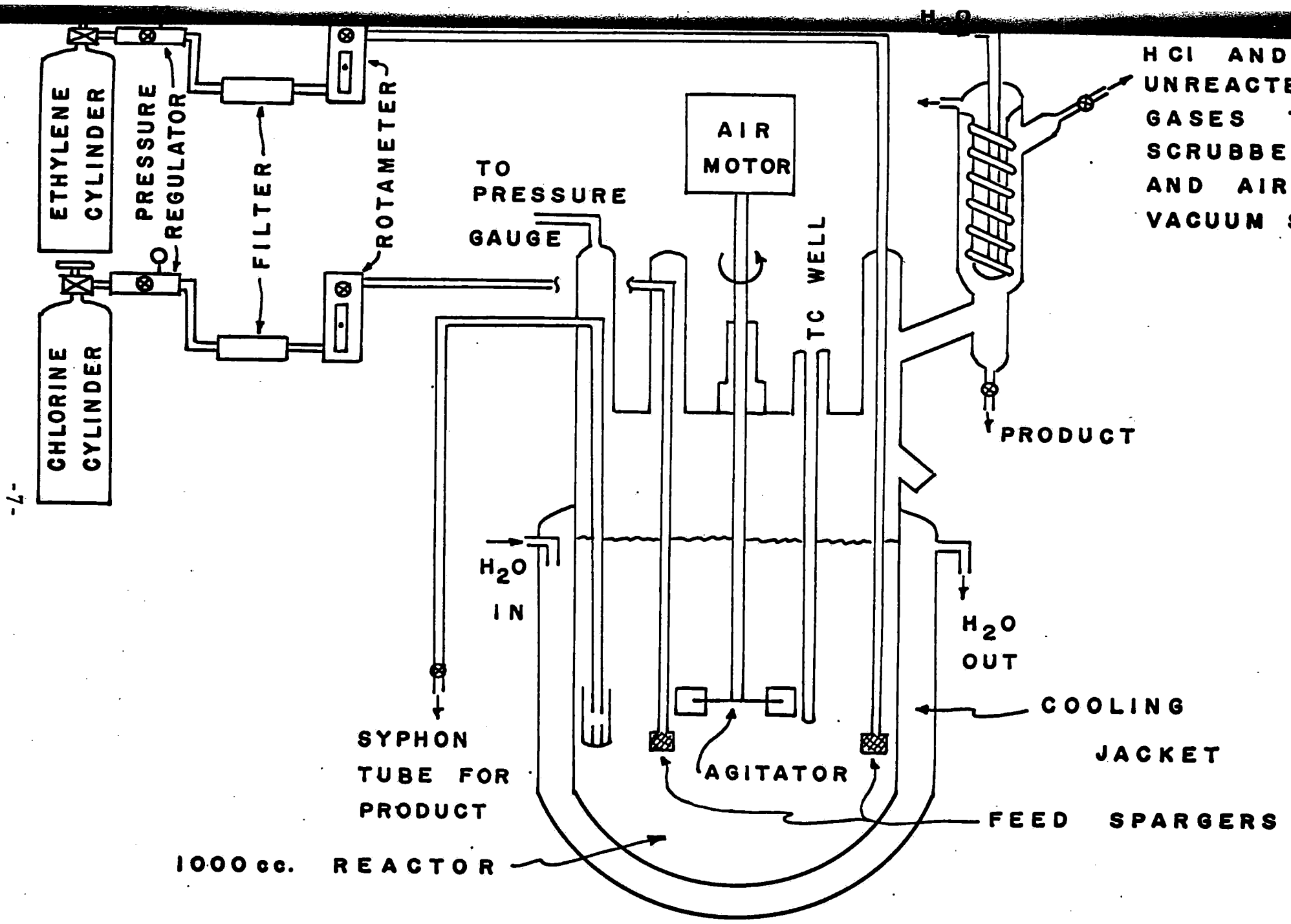


FIG. 1. EXPERIMENTAL APPARATUS USED BY SEATON

The HCl scrubbers were two 500 ml wash bottles arranged in parallel to remove HCl from the exit gas stream. Reactor pressure was regulated by aspirator-air-bleed system. Provision was made for the fine pressure control and to dampen pressure fluctuations.

A heat exchanger was provided to heat the inlet water stream to external jacket.

3. Precedure

Initially the reactor system was purged with nitrogen to remove any traces of water vapor which might contaminate the catalyst and promote undesirable side reactions.

The reactor was operated in two ways: in batch operation, no product was withdrawn during the run; in continuous operation, the product was withdrawn during the run periodically to maintain a constant holdup in the reactor. The initial volume of EDC for batch runs was 1000 cc. For continuous autorefrigerated runs, 800-900 ml was introduced initially which resulted in a 1000 cc operating holdup.

The catalyst, ferric chloride, has an affinity for water vapor. To avoid catalyst degradation by water vapor during weighing and transfer to the reactor, a concentrated solution of $FeCl_3$ in EDC was prepared. This concentrated solution was mixed with pure EDC to obtain a desired catalyst concentration in the initial charge. A catalyst concentration

of 2 g/ℓ was used in most runs.

The agitation speed was maintained in the range of 600-800 RPM which corresponds to 'constant effect region' as observed by Balasubramaniam [8].

Before feeding the reactant gases, the reactor constant was heated to desired operating temperature. This was accomplished by circulating hot water in the jacket in conventionally-cooled runs and by infra-red heat lamp in autorefrigerated runs.

Chlorine feed was begun first. The reactor liquid was saturated with chlorine as evidenced by sudden increase in amount of exit gases. Ethylene feed was then started. Ethylene and chlorine were bubbled through separate glass-spargers.

Typical feed rates were 600 cc/min. Run times were normally 4-6 hours. Cold water was circulated in the condenser.

Yield and conversion results were obtained by measuring the total amount of liquid produced and the amount of HCl evolved during the run. Seaton [2] gives details of operating procedure, equipment design, analytical techniques.

4. Experimental Results of Seaton

Table 1 summarizes the results of all experimental runs. Figure 2 describes the effect of temperature and catalyst

Table 1 - SUMMARY OF EXPERIMENTAL RUNS

Run No.	Cooling Mode	Operating Mode	Sparger Type*1	Catalyst Conc. (gm/1.)	Reactant Feed Rates (cc/hr@ 25°C&1atm)	Reactant Ratio In Feeds Cl_2/C_2H_4	Press. (atm)	Temp. (°C)	Conversion (mole% C_2H_4)	Yield (mole% C_2H_4)
1	Conv.	Batch	P	0	600	1	1	32	92	90
2	Conv.	Batch	P	0	600	1	1	58	81	70
3	Conv.	Batch	P	0	600	1	1	62.5	53	15
4	Conv.	Batch	P	0	600	1	1	67	40	0
5	Conv.	Batch	P	0	600	1	1	75	18	0
6	Conv.	Batch	P	2	600	1	1	32	93.4	93.2
7	Conv.	Batch	P	2	600	1	1	62.5	93	92
8	Conv.	Batch	P	2	600	1	1	80	89	85
9	Auto.	Batch	P	0	600	1	1/4	35-40*2	0	0
10	Auto.	Batch	P	0	600	1	1/2	52-57*2	0	0
11	Auto.	Batch	P	0	600	1	1	74-79*2	15	0
12	Auto.	Batch	P	2	600	1	2/9	40	43	34
13	Auto.	Batch	P	2	600	1	1/2	60	79	71
14	Auto.	Batch	P	2	600	1	1	82.5	86	80
15	Auto.	Batch	S	1	600	1	1	82.5	87	80
16	Auto.	Batch	T	2	600	1	1	82.5	85	76
17	Auto.	Batch	T	4	600	1	1	82.5	85	79
18	Auto.	Batch	S	4	600	1	1	82.5	88	82
19	Auto.	Batch*4	S	9.3*3	600	1	1	82.5	89	83
20	Auto.	Batch*5	P	2	600	1	1	82.5	71	50
21	Auto.	Batch*6	P	2	600	1	1	82.5	80	67
22	Auto.	Batch	P	2	600	1	1	82.5	77	63
23	Auto.	Batch	P	2	600	1.33	1	81	87	56
24	Auto.	Batch	P	2	600	0.9	1	82.5	78	76
25	Conv.	Batch	P	0	1000	1	1	-32	94.2	94
26	Conv.	Batch	P	0	1400	1	1	-32	63	32*8
27	Conv.	Batch	P	2	1000	1	1	32	95	95
28	Conv.	Batch	P	2	1400	1	1	32	96	96
29	Auto.	Batch	P	2	133	1	2/9	40	53	49
30	Auto.	Batch	P	2	300	1	1/2	60	77	74
31	Auto.	Batch	P	2	1000	1	1/2	60	74	63
32	Auto.	Cont.	P	2	300	1	1	82.5	85	83
33	Auto.	Cont.	P	2	1000	1	1	82.5	87	80
34	Auto.	Cont.	P	2	1400	1	1	82.5	88	81
35	Auto.	Cont.*7	P	2	1000	1	1	82.5	87	80

*(Footnotes on next sheet)

Table 1 (continued)

*1 P = porous glass, T = tapered, S = straight tube

*2 The first temperature given is that observed at the beginning of the run. As high-boiling ETC built up in the reactor, the temperature increased. The second temperature given is that observed at the end of the run.

*3 At this concentration, solid undissolved catalyst was present in the reactor.

*4 Both gas feeds introduced together through a common sparger.

*5 Boiling rate increased by heat lamp.

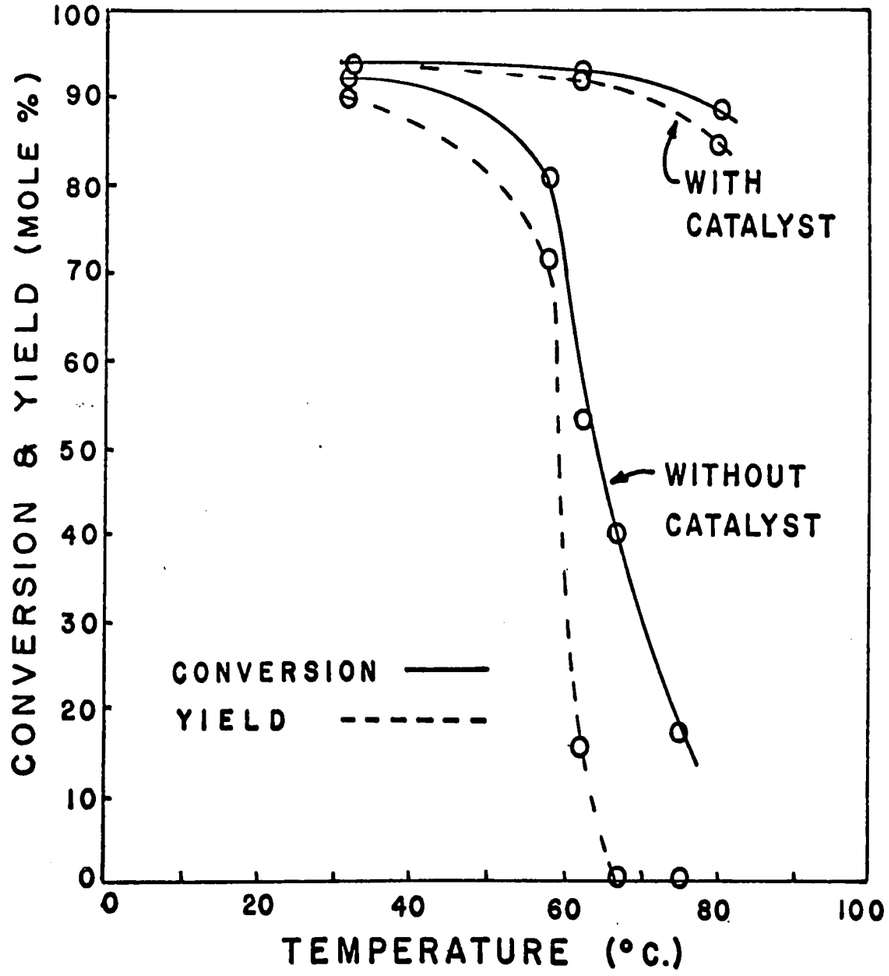
*6 Boiling rate increased by hot water in jacket.

*7 Reactor volume 1500 cc.

*8 The substitution reaction rate increased with time.

FIG. 2. EFFECT OF TEMPERATURE ON OBSERVED CONVERSION AND YIELD OF ETHYLENE WITH AND WITHOUT CATALYST FOR CONVENTIONALLY COOLED REACTOR

OPERATING PRESSURE: 1 atm.
FEED RATE: 600 ccPM @ 25°C, 1 atm.
STARTING VOLUME OF LIQUID: 1000 ml.
INITIAL CATALYST CONCENTRATION: 2.0g/ℓ of $FeCl_3$
LENGTH OF RUNS: 5-6 hrs.



presence on conversion and yield when conventional cooling was employed. Yield and conversion drop off very sharply after about 58°C, when no catalyst was used. This agrees well with the observations of Balasubramaniam et al. [8] that temperature variation in the range of 80-56° did not significantly alter the reactor performance. The runs made with catalyst show a very slight decrease to conversion and yield with increase in temperature. All these runs were made at atmospheric pressure. Gaseous feed rates of both reactants were maintained at 600 ccPM. Run times were 5-6 hours.

Figure 3 shows the effect of temperature and catalyst on conversion and yield during autorefrigerated batch runs. In autorefrigerated runs, the reactor pressure varied with temperature. Feed rates and run times were the same as previous runs. Conversion increased rapidly with temperature (and pressure) when catalyst was used. These runs indicate a marked change in mechanism when catalyst was used. Reactor productivity was very low when no catalyst was used. Large amounts of HCl evolved during these runs. When no catalyst was used, the amount of EDC left at the end of the run was less than the amount charged initially.

Figure 4 describes the effect of catalyst concentration on reactor performance during autorefrigerated batch runs. All runs were made at 1 atm (82.5°C), 600 cc pm feed rates

FIG. 3. EFFECT OF TEMPERATURE ON OBSERVED CONVERSION AND YIELD OF ETHYLENE WITH AND WITHOUT CATALYST FOR AUTOREFRIGERATED REACTOR

FEED RATE: 600 ccPM @ 25°C, 1 atm.
STARTING VOLUME OF LIQUID: 1000 ml.
INITIAL CATALYST CONCENTRATION: 2.0g/ℓ of $FeCl_3$
LENGTH OF RUNS: 5-6 hrs.

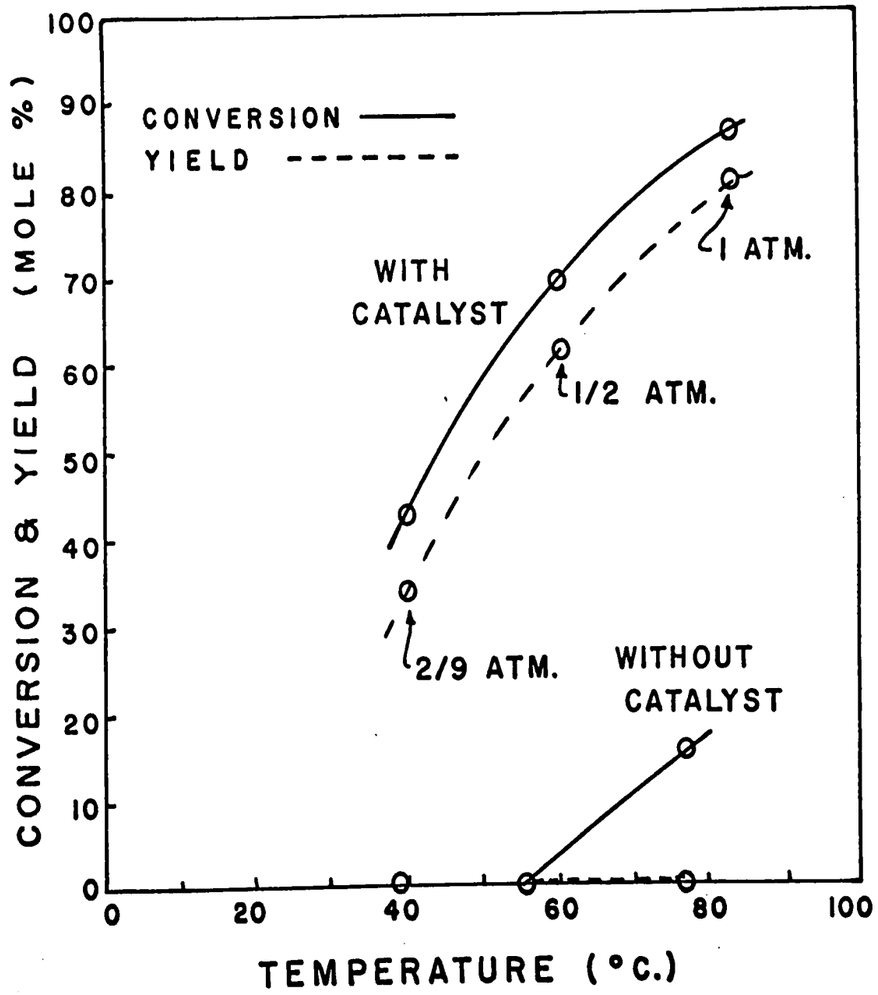
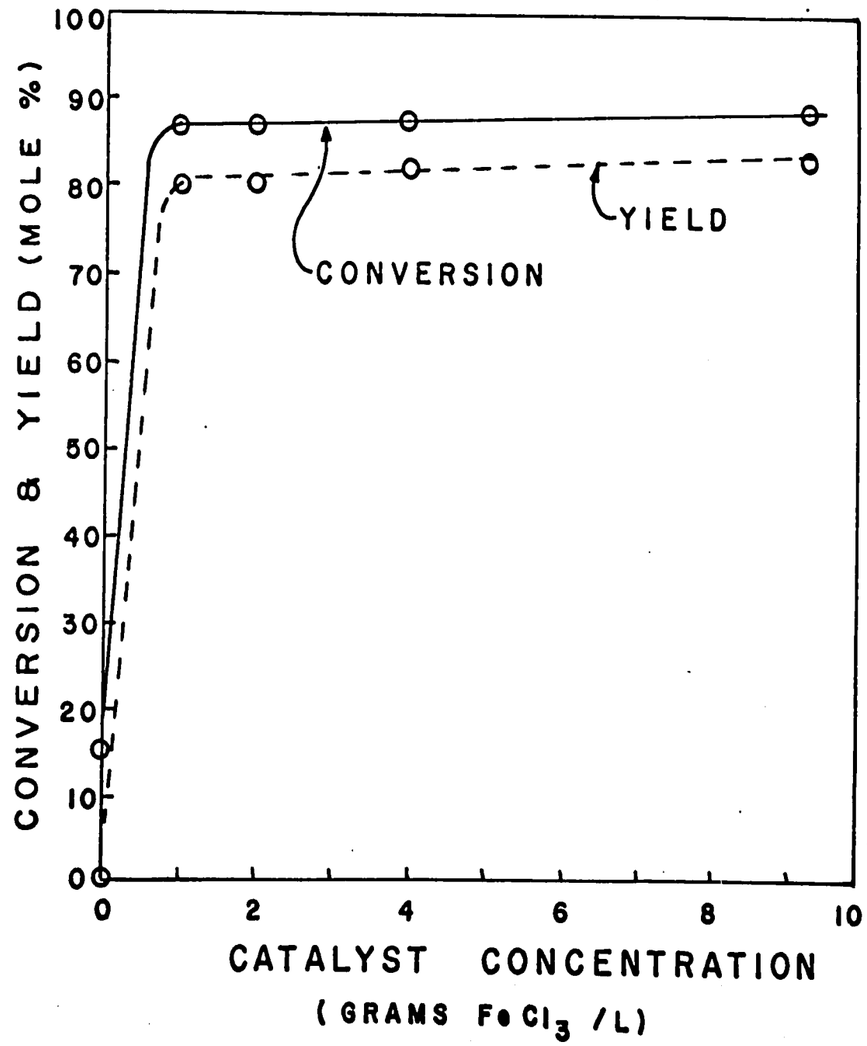


FIG. 4. EFFECT OF CATALYST CONCENTRATION ON OBSERVED CONVERSION AND YIELD OF ETHYLENE

OPERATING PRESSURE: 1 atm.
FEED RATE: 600 ccPM @ 25°C, 1 atm.
STARTING VOLUME OF LIQUID: 1000 ml.
LENGTH OF RUNS: 5-6 hrs.
COOLING MODE: Autorefrigeration



of reactant gases. Although catalyst presence is mandatory for high yield, catalyst concentration greater than 1-2 g/ℓ had little effect on reactor productivity. Fouling of feed sparger tubes was experienced when catalyst concentration was increased. Three types of spargers were tested to reduce the clogging of the feed spargers which limited the feed rates. The normal spargers were porous cylindrical glass bulbs, 12 mm in outside diameter and 20 mm long. Tapered glass spargers were also used (1.5 mm inside diameter at the tip and straight tubes were 5 mm inside diameter). The type of sparger had only a slight effect on conversion and yield.

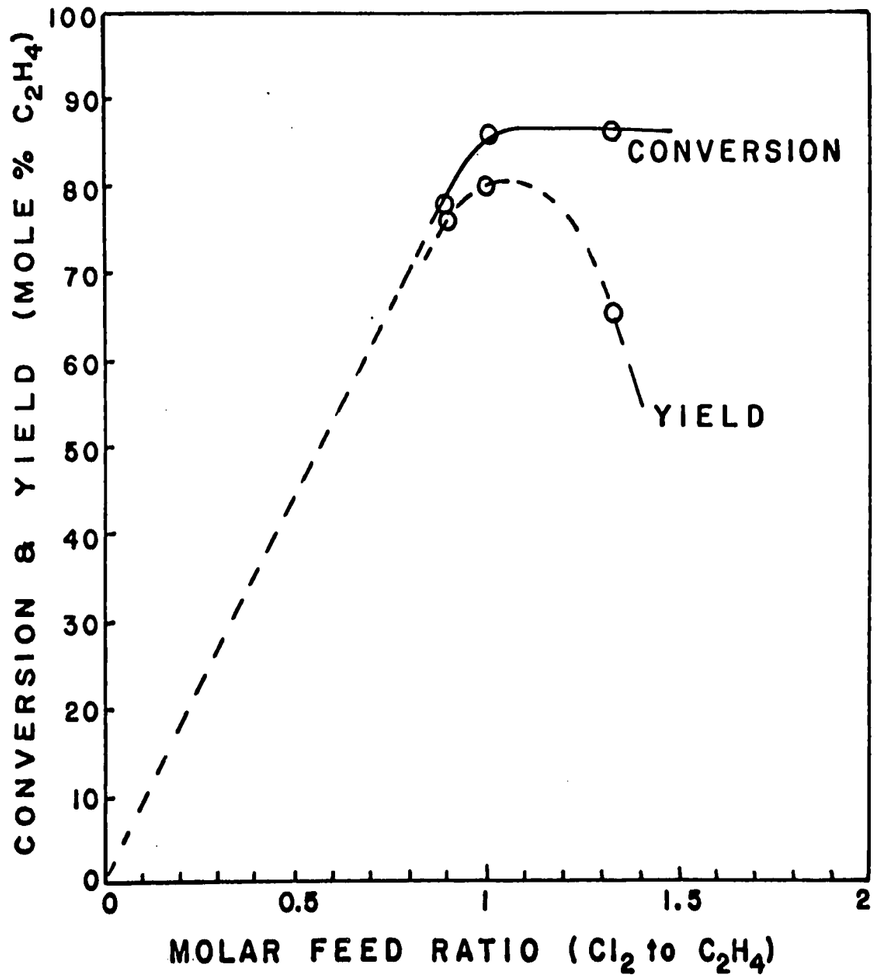
When the reactant gases were fed together from the same sparger a significant drop in conversion and yield and an increase in substitution were also observed (run no. 20). Increasing the rate of boiling by adding heat to the autorefrigerated reactor (run no. 21) reduced yield.

Figure 5 described the effect of reactant feed ratio on reactor productivity in the autorefrigerated runs. Chlorine/ethylene ratio greater than one produced high amounts of the undesirable by-product ETC and reduced EDC yield.

The last series of runs explored the effect of feed rate. Ethylene superficial velocity was defined as volumetric flow rate of ethylene per unit free cross-sectional area of the reactor. Reaction rate was defined as rate of

FIG. 5. EFFECT OF MOLAR FEED RATIO ON OBSERVED CONVERSION AND YIELD OF ETHYLENE.

OPERATING PRESSURE: 1 atm.
FEED RATE: 600ccPM @ 25°C, 1 atm.
STARTING VOLUME OF LIQUID: 1000 ml.
INITIAL CATALYST CONCENTRATION: 2.0g/ℓ of $FeCl_3$
LENGTH OF RUNS: 5-6 hrs.



consumption of ethylene. Table 2 summarizes the results.

Figure 6 shows a plot of reaction rate versus ethylene superficial velocity for the conventionally cooled reactor at 32°C and 1 atm and for the autorefrigerated reactor at three temperatures and pressures.

Although reaction rate varies with ethylene superficial velocity, conversion did not change much. Thus a constant fraction of total feed was converted at any feed rate in the range described. The slopes of the lines of experimental data in Figure 6 are all approximately one, unlike the data of Balasubramaniam et al. [8] which showed a slope of 2/3.

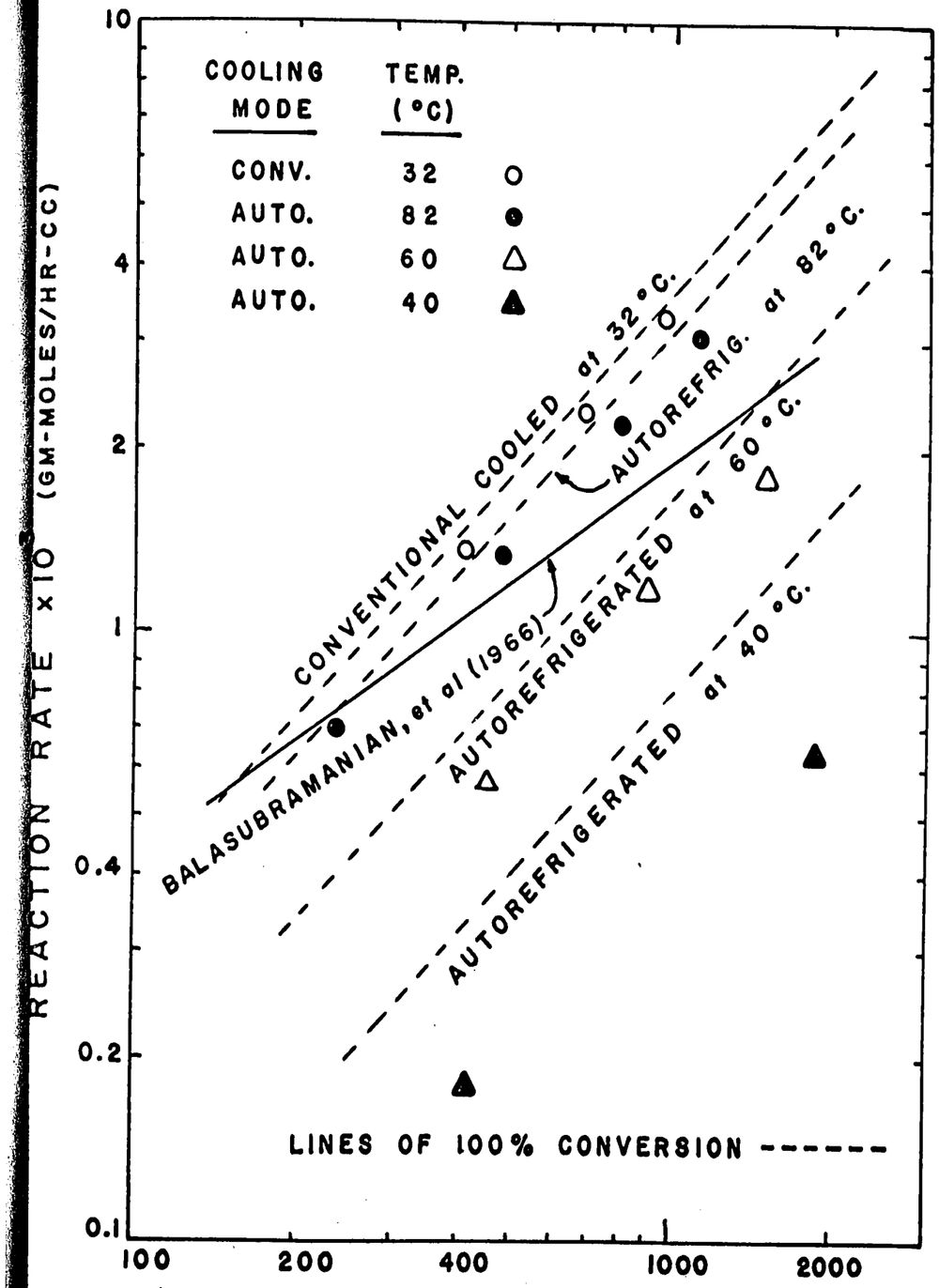
Table 2 - DATA AT VARIOUS GAS VELOCITIES

Run No.	Ethylene Feed Rate (cc/min @ 25°C&1atm)	Conversion (mole%)	Yield (mole%)	Ethylene Superficial Velocity (cm/hr)	Reaction Rate x10^3 (gm-moles /hr-cc)	Cooling Mode	Catalyst Conc. (gm/l.)	Temp. (°C.)	Pressure (atm.)
1	600	92	90	410	1.35	Conv.	0	32	1
25	1000	94.2	94	684	2.33	Conv.	0	32	1
26	1400	63	32	960	2.19*1	Conv.	0	32	1
6	600	93.4	93.2	410	1.39	Conv.	2	32	1
27	1000	95	95	684	2.34	Conv.	2	32	1
28	1400	96	95	960	3.31	Conv.	2	32	1
29	133	53	49	420	0.18	Auto.	2	40	2/9
12	600	43	34	1870	0.63	Auto.	2	40	2/9
30	300	77	74	448	0.57	Auto.	2	60	1/2
13	600	79	71	895	1.18	Auto.	2	60	1/2
31	1000	74	63	1490	1.82	Auto.	2	60	1/2
32	300	85	83	238	0.70	Auto.	2	82	1
14	600	86	80	477	1.35	Auto.	2	82	1
33	1000	87	80	795	2.21	Auto.	2	82	1
34	1400	88	81	1115	3.08	Auto.	2	82	1
35*2	1000	87	80	795	1.48	Auto.	2	82	1

*1 The operation of the conventionally cooled reactor without catalyst at this high flow rate was very irratic, indicating a stability problem. The results of this run are, therefore, of questionable accuracy.

*2 Reactor Volume was 1500 cc.

FIG. 6. EFFECT OF ETHYLENE SUPERFICIAL VELOCITY ON REACTION RATE



IV. PRELIMINARY CONSIDERATIONS

1. Conventional Cooling Model

Balasubramaniam et al. [8] studied the kinetics of ethylene dichloride formation in a conventionally cooled stirred tank reactor. The experimental runs were conducted at 1 atm pressure, 32°C and without catalyst. A diffusion-controlled liquid film model was shown to be consistent with the experimental data. In developing the mass tranfer limited model, the following principal assumptions were made.

1) The liquid phase reaction between ethylene and chlorine is instantaneous and irreversible. The latter is based on thermodynamic considerations.

2) Bubble coalescence, even if present, is negligible.

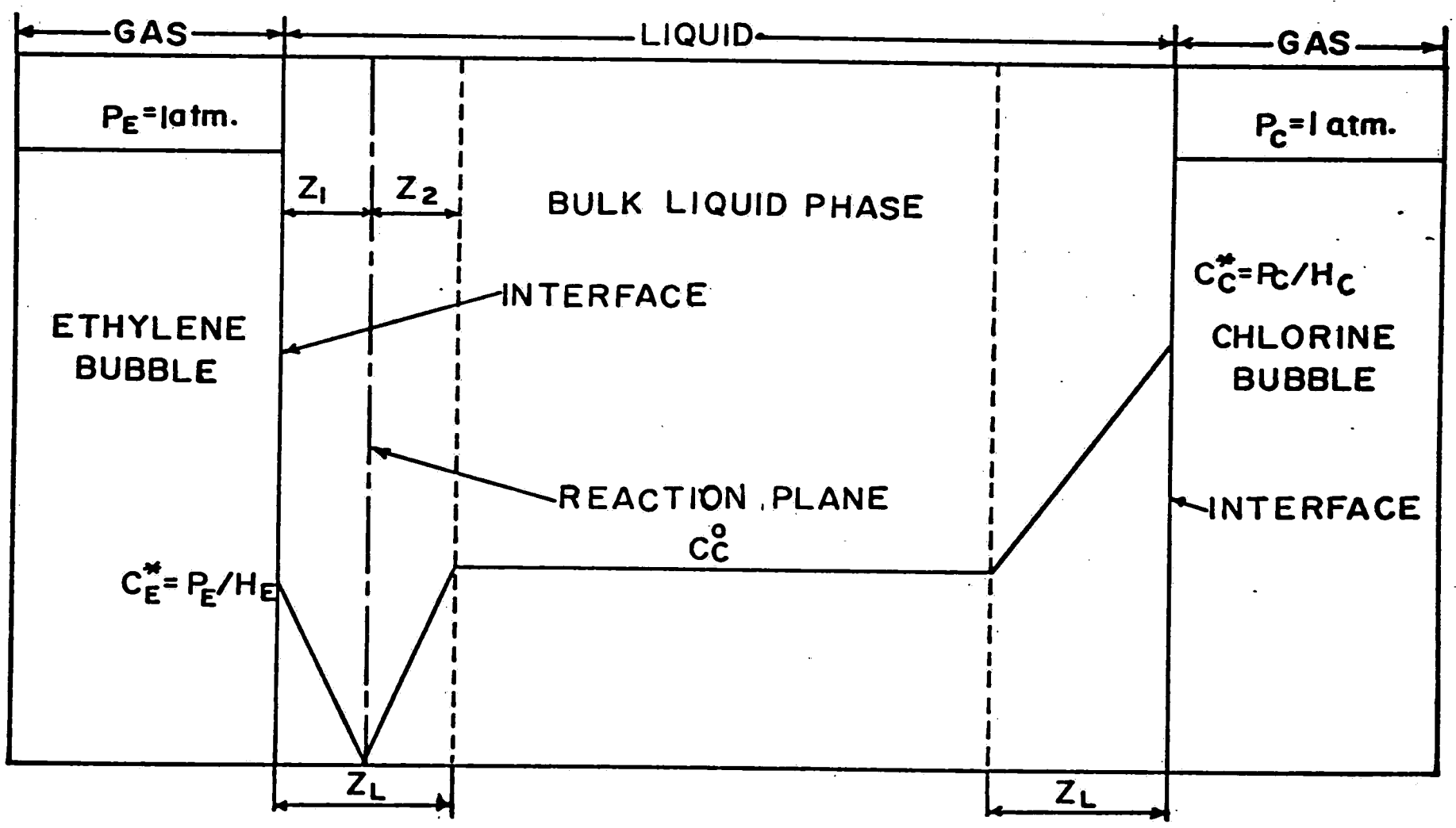
3) The mass transfer coefficients of ethylene and chlorine are not influenced by presence of bubbles of other gas.

4) At equal superficial velocities, the film thickness and the total interfacial areas of ethylene and chlorine bubbles are equal.

5) The side reaction effects are negligibly small.

As shown in Figure 7, the film theory model by Balasubramaniam presumed existence of two liquid films of finite thickness adjacent to the gas-liquid interfaces. Ethylene diffuses through the liquid film on the left to

FIG. 7. FILM THEORY MODEL OF CHLORINE-ETHYLENE REACTION IN THE PRODUCT ETHYLENE DICHLORIDE per BALASUBRAMANIAM et. al.



meet chlorine diffusing in opposite direction from the bulk liquid. The reaction plane RR' moves away from the gas-liquid interface and reaches an equilibrium position in a very short time. At this equilibrium position, the molar diffusion rates of ethylene and chlorine are equal. Due to instantaneous reaction, the ethylene and chlorine concentrations at the reaction plane are zero. Chlorine diffuses through the liquid film to the bulk liquid phase. If chlorine transfer from the bulk liquid phase to the bulk vapor phase (the vapor above the liquid surface, not in chlorine or ethylene bubbles) is negligible, the steady state diffusion rate of chlorine from chlorine bubbles to the bulk liquid phase should equal the diffusion rate of chlorine from the bulk liquid phase to the reaction plane in the liquid film adjacent to ethylene gas-liquid interface.

Assuming that the molar concentrations of ethylene and chlorine are very low at the reaction plane and in the liquid film:

$$N_E = K_E(C_E^*-0) = \frac{D_E}{Z_1} \times C_E^* \qquad (1)$$

$$-N_C = K_C(C_C^\circ-0) = \frac{D_C}{Z_2} \times C_C^\circ \qquad (2)$$

where

N_E = molar flux of ethylene to the reaction plane from ethylene bubbles.

N_C = molar flux of chlorine to the reaction plane from the bulk liquid phase.

C_E^* = interfacial concentration of ethylene at ethylene-bulk liquid interface.

C_C° = bulk liquid concentration of chlorine.

K_E and K_C are mass transfer coefficients for ethylene and chlorine.

D_E and D_C are diffusivities of ethylene and chlorine in EDC.

Z_1 and Z_2 are shown in Figure 7.

Assuming equimolal diffusion of ethylene and chlorine at the reaction plane ($N_E=-N_C$) , combining equation (1) and equation (2).

$$N_E = \frac{D_E \times C_E}{Z_L}\left(1 + \frac{D_C}{D_E} \times \frac{C_C^*}{C_E^*}\right) \qquad (3)$$

where

$$Z_L = Z_1 + Z_2 .$$

Assuming Henry's law constants (H_E and H_C) independent of solute concentrations

$$C_E^* = P_E/H_E \qquad (4)$$

$$C_C^* = P_C/H_C \qquad (5)$$

where P_E and P_C are partial pressures of ethylene and chlorine in the ethylene and chlorine bubbles respectively.

The rate of solution of chlorine from chlorine bubbles to the bulk liquid phase is

$$-N_C^* = N_E = \frac{D_C}{Z_L}(C_C^* - C_C^\circ) . \qquad (6)$$

By defining the interfacial area per unit volume as "a", Balasubramaniam expressed reaction rate as

$$R = N_E \times a \quad . \tag{7}$$

Combining equation (3), equation (4), equation (5), equation (6) and equation (7):

$$R = \frac{1}{2} K_E^1 \cdot P_E \left\{ \frac{1}{H_E} + \frac{D_C}{D_E} \cdot \frac{P_C}{P_E} \cdot \frac{1}{H_C} \right\}$$

where $K_E^1 = D_E / Z_L$.

Balasubramaniam found that mass transfer coefficient K_E^1 , was related to ethylene superficial velocity by

$$K_E^1 \propto V_S^{2/3} \quad .$$

The Henry's law constants were determined experimentally at 32°C and 1 atm, P_E and P_C were set equal to 1 atm, the reactor operating pressure and the diffusivities were calculated using Wilke-Chang equation. Reaction rate could be expressed as a function at gas velocity.

$$R = K V_S^{2/3}$$

where K is a constant.

This contradicts Seaton's finding that the reaction rate was directly proportional to ethylene superficial velocity.

Desai [9] studied the gas-liquid kinetics of chlorination of acetylene to produce tetrachloroethane. The reaction

system was:

$$C_2H_{4(g)} + 2Cl_2 \text{ (dissolved)} \rightarrow C_2H_2Cl_4 - 103 \text{ kcal/mole} .$$

Ethylene was bubbled in the product tetrachloroethane. The experimental runs were made at 1 atm pressure and at temperatures 40°C and 80°C. Antimony pentachloride and ferric chloride were tested as catalysts.

It was found that the reaction rate was independent of catalyst concentration and temperature. Physical mass transfer coefficient were related to superficial gas velocity by

$$K^l \propto V_S^{1.1} .$$

These experimental findings are close to Seaton's experimental findings.

2. Mass Transfer Model

An important aspect of reaction system under investigation is mass transfer between gas phase and liquid phase. The reactant gases are absorbed in the liquid phase prior to the reaction. The reactant gas bubbles would be diluted due to EDC evaporation within bubbles. Absorption/desorption of chlorine, absorption of ethylene and EDC vaporization are possible at the interface between the bulk vapor phase and the bulk liquid phase. Selecting a suitable mass transfer model is necessary to develop a mathematical model for the reaction system under study.

In case of the absorption of reactant gases, the overall mass transfer resistance is sum total of the diffusion resistance experienced in the gas phase (bubbles) and the diffusion resistance experienced in the liquid phase. Based on the observations made in reference [8] and reference [3], the diffusion resistance within bubbles is negligibly small compared to liquid phase diffusion resistance. Calderbank et al. [3] states, "The small diffusion path offered by comparatively small bubbles found in aerated mixing vessels, together with high diffusion coefficients as compared with those obtaining in the liquid phase coupled with the effect of turbulence in the gas bubbles, combine to make the (gas-film) mass transfer resistance negligible compared with liquid phase resistance."

Hence considering the diffusion resistance within gas bubbles negligible, the vapor composition could be assumed to be uniform within the bubbles. The interfacial concentration of reactant gases is related to the partial pressure of reactant gases by Henry's law constant.

The liquid phase diffusion resistance is represented by the film model. It pictures a stagnant film at the surface of the liquid next to the gas bubbles. The hydrodynamic property of the system is accounted by the thickness of the film.

The film model is preferred over other models in view of the simplicity it offers while incorporating the essential

feature of the real system that the gas must get into liquid by solution before it can be transported by convection. Danckwerts [2] states, "Although film model is not very realistic, predictions based on film models are usually remarkably similar to those based on more sophisticated models and sometimes identical. In many cases, the difference between predictions based on the basis of these models will be less than the certainty about the values of physical quantities used in the calculation."

Physically, the assumption of negligible vapor phase diffusion resistance means the reactant gas bubbles grow in size immediately as they contact the liquid phase due to EDC evaporation at the gas liquid interface. The bubble is broken into many smaller bubbles by agitation. If its size grows beyond the critical bubble size, EDC evaporates into the bubbles until the partial pressure of EDC in the bubbles correspond to the vapor pressure of EDC at the reactor operating temperature. For practical purposes, this step could be assumed to be accomplished in a very short time. Next, as the reactant gas bubbles shrink due to reactant gas absorption, EDC would condense at such a rate that EDC partial pressure within bubbles would remain equal to EDC vapor pressure at the reactor operating temperature. HCl evolved might diffuse from the reaction zone to ethylene bubbles and/or form new bubbles in the liquid phase.

Similarly, the partial pressure of EDC in the bulk vapor phase would be equal to the EDC vapor pressure at the reactor operating temperature. This is reasonably accurate because the reactant gases are sparingly soluble in the EDC and the reactor operating pressures are low. (Roult's law states

$$P_{EDC} = P^{V}_{EDC} \times X_{EDC} , \qquad X_{EDC} \simeq 1.0 \rightarrow P_{EDC} = P^{V}_{EDC} .)$$

Similarly, the partial pressure of EDC in the condenser should be equal to the vapor pressure of EDC at the reflux temperature (provided the temperature of exit gas stream equals the reflux temperature).

3. EDC Loss from Condenser

The unreacted gases and HCl evolved have to be continuously purged to maintain constant pressure during the steady state operation. Some of the EDC vapor entering the condenser is lost via the exit gas stream from the condenser to the HCl absorbers. The partial pressure of EDC is equal to the vapor pressure of EDC at the exit gas stream temperature.

Seaton calculated the conversion and yield data from the amount of EDC produced and HCl evolved during the run. He did not take into account the EDC loss from the condenser. On detailed calculations it was found EDC loss could be significant especially during experimental runs at low pressures.

Seaton assumed that the substitution reaction producing ETC and HCl gas were the only significant side reactions.

Thus, total moles of ETC formed is equal to the total moles of HCl evolved during the run. If n_2 moles of HCl were collected, the weight of ETC formed during the run would be:

$$W_2 = n_2 \times M_2$$

where M_2 - mol. wt. of ETC.

The actual weight of EDC formed during the run was therefore

$$W_1 = W_p - W_2$$

where W_p is an increase in weight of reactor content during the run.

The moles of EDC produced:

$$n_1 = W_1/M_1$$

where M_1 = mol. wt. of ETC.

The moles of ethylene reacted would be

$$n_p = n_1 + n_2 .$$

If n_f were the total moles of ethylene fed into the reactor during the run,

$$C = \text{conversion of ethylene} = n_p/n_f$$

$$Y = \text{yield of ethylene} = n_1/n_f .$$

Seaton's calculations of conversion and yield data did

not take into account product loss via the condenser.

If C' and Y' represent actual conversion and yield and F_E and F_C are feed flow-rates of ethylene and chlorine respectively,

$$\text{Rate of ethylene loss via condenser} = F_E(1-C') \quad (8)$$

$$\text{Rate of chlorine loss via condenser} = F_C - F_E(2C'-Y') \quad (9)$$

$$\text{Rate of HCl loss via condenser} = F_E(C'-Y') \ . \quad (10)$$

As mentioned earlier, P''_{ED} , the partial pressure of EDC in the exit gas stream is equal to EDC vapor pressure at the temperatures of the exit gas stream

$$\frac{\text{Rate of EDC vapor loss}}{\text{Rate of ethylene plus chlorine plus HCl loss}} = \frac{P''_{ED}}{(P-P''_{ED})} \quad (11)$$

Combining equation (8), equation (9), equation (10) and equation (11):

$$\text{Rate of EDC loss} = \frac{P''_{ED}}{(P-P''_{ED})} \{F_C+F_E(1-2C')\} \ .$$

Since the total moles of EDC plus ETC left in the reactor is equal to the total moles of EDC plus ETC formed minus the EDC lost via condenser.

$$F_E \times C = F_E \times C' - \frac{P''_{ED}}{(P-P''_{ED})} \times \{F_C+F_E(1-2C')\} \ .$$

On simplification,

$$C = C'\left\{1 + \frac{2P''_{ED}}{(P-P''_{ED})}\right\} - \frac{P''_{ED}}{(P-P''_{ED})}\left\{\frac{F_C}{F_E} + 1\right\} \ . \quad (12)$$

Similarly

$$Y = Y' - \frac{P''_{ED}}{(P-P''_{ED})}\left\{\frac{F_C}{F_E} + 1 - 2C'\right\} .$$

The temperature of the cold water being circulated in the condenser is 8-10°C.

Figures 8 and 9 are plots of observed conversion of ethylene (neglecting EDC loss from condenser) versus actual conversion of ethylene when the temperature of the exit gas stream is assumed 15°C and 20°C respectively.

These plots indicate that EDC vapor loss from condenser increases rapidly as the operating pressure decreases and as the temperature of the exit gas stream increases.

The negative values of observed conversion of ethylene indicate that the moles of EDC lost from condenser is greater than the moles of EDC plus ETC formed by the reaction. This means less moles of EDC plus ETC would be left at the end of the run than moles of EDC charged initially. This explains Seaton's observation that during some experimental runs, less moles of EDC plus ETC was left than moles of EDC charged initially.

Table 3 shows Seaton's experimentally observed conversion and yield of ethylene and corresponding corrected conversion and yield of ethylene adjusted for EDC loss from condenser.

FIG. 8. EFFECT OF OPERATING PRESSURE ON EDC LOSS FROM CONDENSER AT CONDENSER REFLUX TEMPERATURE OF 15°C

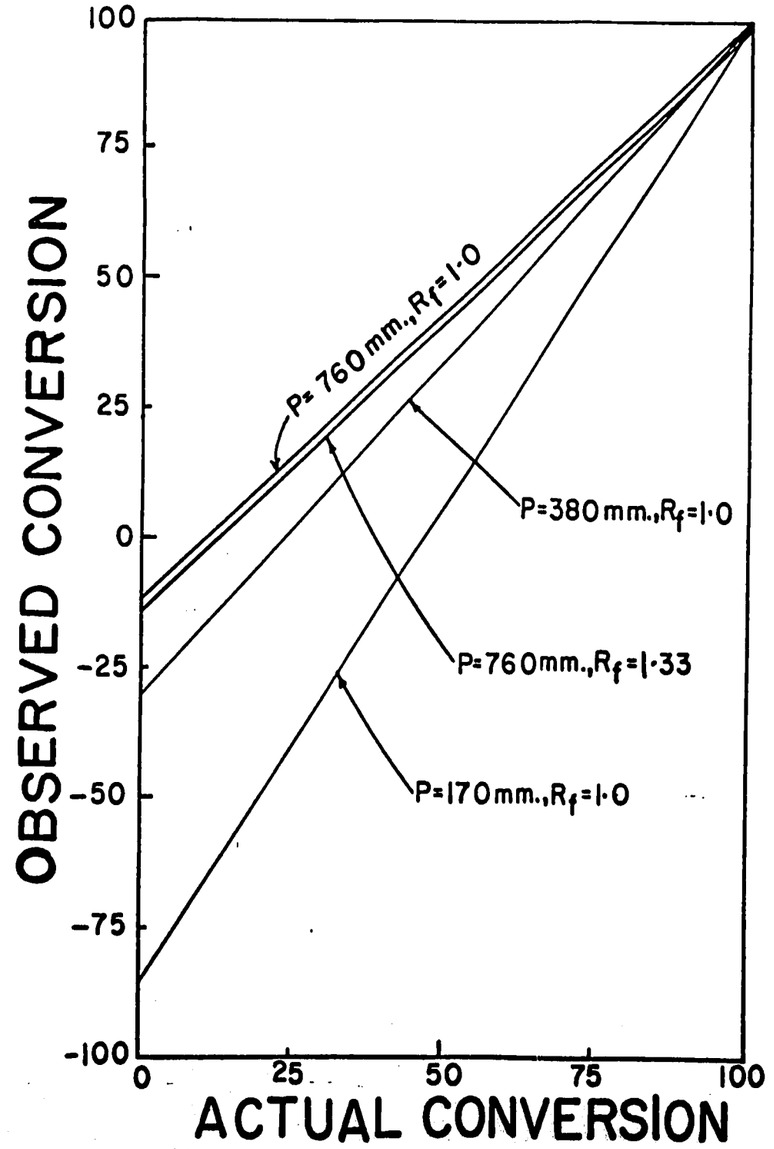


FIG. 9. EFFECT OF REACTOR PRESSURE ON EDC LOSS FROM CONDENSER AT CONDENSER REFLUX TEMPERATURE OF 20°C

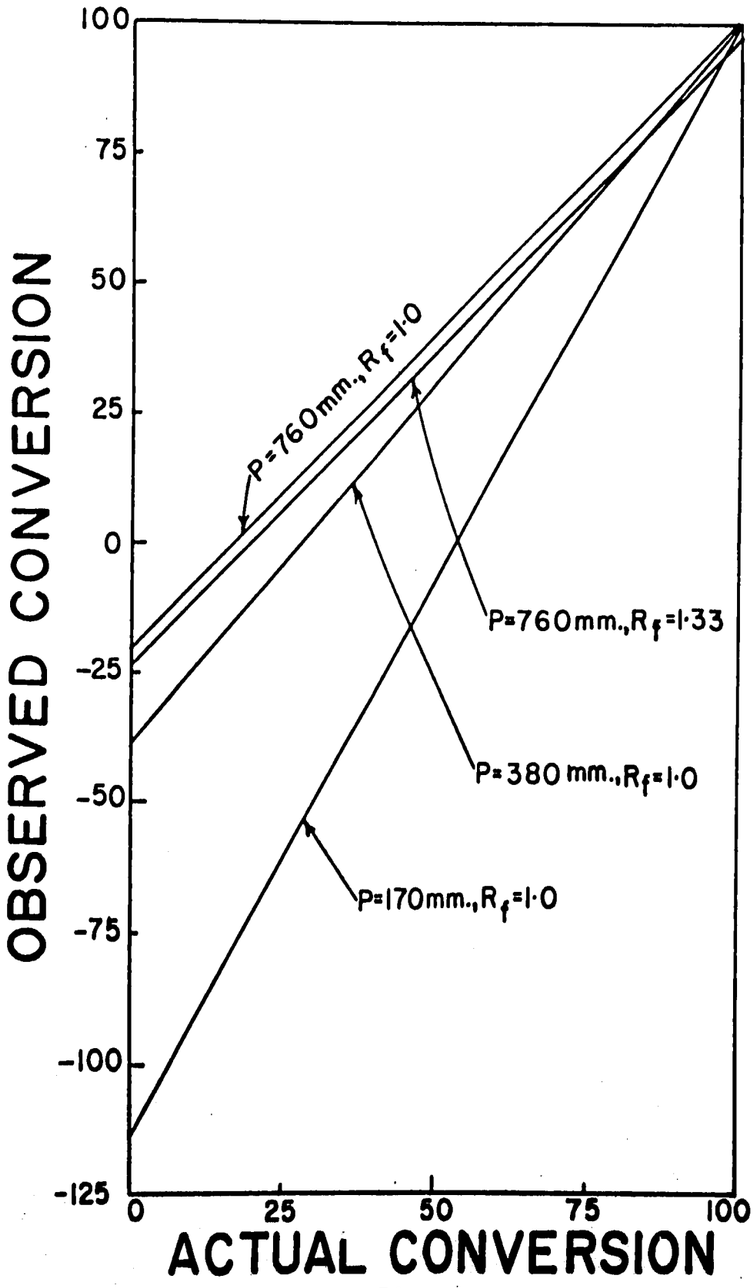


Table 3 - CORRECTED EXPERIMENTAL DATA

S. No.	1	2	3	4	5	6
Exptl. Run No.	1	25	6	27	28	29
Cooling Mode	Conv.	Conv.	Conv.	Conv.	Conv.	Auto.
Operating Mode	Batch	Batch	Batch	Batch	Batch	Batch
Sparger Type	P	P	P	P	P	P
Catalyst Conc. (g/ℓ)	0.0	0.0	.0	2.0	2.0	2.0
Ethylene Feed Rate (cc/min) @ 25°C, 1 atm.	600.	1000.	600.	1000.	1400.	133.
Reactant Feed Ratio Cl_2/C_2H_4	1.0	1.0	1.0	1.0	1.0	1.0
Operating Temperature (°C)	32.0	32.0	32.0	32.0	32.0	40.0
Operating Pressure (atm.)	1.0	1.0	1.0	1.0	1.0	2/9
Condenser Reflux Temperature (°C)	12.0	12.0	12.0	12.0	12.0	27.0
Observed Conversion (mole % of Ethylene)	92.0	94.2	93.4	95.0	96.0	53.0
Observed Yield (mole % of Ethylene)	90.0	94.	93.2	95.0	96.0	49.0
Corrected Conversion (mole % of Ethylene)	92.88	94.84	94.13	95.55	96.44	85.95
Corrected Yield (mole % of Ethylene)	90.88	94.64	93.93	95.55	96.44	81.95

7	8	9	10	11	12	13	14	15
12	2	30	13	31	3	7	8	23
Auto.	Conv.	Auto.	Auto.	Auto.	Conv.	Conv.	Conv.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	P	P	P	P	P	P	P	P
2.0	0.0	2.0	2.0	2.0	0.0	2.0	2.0	2.0
600.	600.	300.	600.	1000.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.33
40.0	58.0	60.0	60.0	60.0	62.5	62.5	80	81
2/9	1.0	1/2	1/2	1/2	1.0	1.0	1.0	1.0
28.5	12.0	15.0	8.0	15.0	13.0	13.0	34.0	34.0
43.0	81.0	77.0	79.0	74.0	53.0	93.0	89.0	87.0
34.0	70.0	74.0	71.0	63.0	15.0	92.0	85.0	56.0
85.0	83.09	82.52	82.09	79.97	58.43	93.81	92.04	95.40
76.0	72.09	79.52	74.09	68.97	20.43	92.81	88.04	64.40

16	17	18	19	20	21	22	23	24
14	15	16	17	18	19	33	34	35
Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Cont.	Cont.	Cont.
P	S	T	T	S	S	P	P	P
2.0	1.0	2.0	4.0	4.0	9.3	2.0	2.0	2.0
600.	600.	600.	600.	600.	600.	1000.	1400.	1000.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
48.0	43.0	43.0	50.0	41.5	39.0	43.0	41.0	43.0
86.0	87.0	85.0	85.0	88.0	89.0	87.0	88.0	87.0
80.0	80.0	76.0	79.0	82.0	83.0	80.0	81.0	80.0
92.40	92.08	90.86	92.28	92.40	92.40	92.08	92.40	92.08
86.40	85.08	87.86	86.28	82.40	82.40	85.08	82.40	85.08

4. Equilibrium Temperature in Autorefrigerated Reactor

In the autorefrigerated runs, Seaton found that the operating temperature was slightly below the boiling point of EDC at the corresponding operating pressure, and that it was influenced by the catalyst presence and feed ratio to a small extent.

The reactor could be divided into two distinct zones: the bulk vapor phase and the bulk liquid phase. The unreacted gases and HCl continuously escape from the bulk liquid phase to the bulk vapor phase along with EDC vapor. Gas leaves the bulk vapor phase, flowing into the condenser. It is possible that some reactions between ethylene, chlorine and EDC occur in the bulk vapor phase. EDC vaporizes or condenses in the bulk vapor phase such that the partial pressure of EDC in the bulk vapor phase is equal to EDC vapor pressure at the reactor temperature. The reaction between ethylene and chlorine commences as soon as ethylene feed is begun. (EDC is saturated with chlorine.) The heat generated in the reactor depends on the ethylene reaction rate primarily. If the heat generated due to the reactions is greater than the heat used in EDC evaporation and to heat up the reactant feed gases and the reflux to the reactor temperature plus atmospheric heat losses, the temperature of the reactor tends to rise. When they are equal, steady state is attained.

The partial pressure of EDC (P'_{ED}) in the reactor exit gas stream to the condenser is equal to EDC vapor pressure at the reactor temperature. The amount of EDC vapor going to the condenser is equal to $(P'_{ED}/P-P'_{ED})$ times the total amount of unreacted gases and HCl going to the condenser via the reactor exit gas stream. The factor $(P'_{ED}/P-P'_{ED})$ would change very rapidly with temperature compared to the latter (C and Y do not change very rapidly with temperature) particularly when the reactor temperature is in the vicinity of the EDC boiling point temperature at the operating pressure. The net effect would be an increase in EDC vapor flow rate to the condenser with an increase in the reactor temperature.

As the reactor temperature rises, the rate of heat consumption rises, the rate of heat consumption due to EDC vaporization also increases. A steady state is reached when the heat generated due to the reactions equals the sum of atmospheric heat losses, heat used in heating up the incoming streams to the reactor temperature and heat used in EDC evaporation.

Consider two experimental runs in which the reactant feed rates were the same. However, the conversion and yield of ethylene observed in the first run were higher than that in the second run. At steady state operation, the heat generated would be higher in the former case. Since the atmospheric heat losses and heat used to heat up the incoming streams to the reactor temperature would not differ much in

the two experimental runs, the rate of EDC evaporation would be higher in the first run. However the total amount of unreacted gases and HCl leaving the condenser would be higher in the second experimental run. This implies, the factor $P'_{ED}/(P-P'_{ED})$ would be considerably higher in the first experimental run. Hence, the equilibrium temperature would be higher in the first experimental run when higher conversion and yield were observed. This is consistent with Seaton's observation that higher equilibrium operating temperatures were encountered in the catalyzed autorefrigerated runs as compared to the noncatalyzed autorefrigerated runs. Higher conversions of ethylene were observed in the catalyzed autorefrigerated runs.

Consider two experimental runs when conversions and yields of ethylene were nearly equal and the reactant feed rates were different. More heat generation, hence, more EDC evaporation would occur in the experimental run with higher feed rate. The ratio of amounts of EDC evaporated in the two runs would be equal to the ratio of ethylene feed rates in the two experimental runs. The ratio of total amount of unreacted gases and HCl evolved, would also equal the ratio of ethylene feed rates (atmospheric heat losses negligible). This implies, the factor $P'_{ED}/(P-P'_{ED})$ would be equal to both experimental runs; hence, the same equilibrium operating temperature in both the cases. This is reasonable in light of Seaton's experimental data (Run No. 6, 27 and 28).

Consider two experimental runs when the conversion and yield of ethylene were approximately the same. However, excess of either reactant gas is used in one of the experiments. The flow rate of EDC vapor to the condenser would be the same in both cases. However the total amount of unreacted gases and HCl would be much higher when excess of either reactant gas is used. This means the factor $P'_{ED}/(P-P'_{ED})$ would be lower when excess of either reactant gas is used. The equilibrium operating temperature would be lower if excess of either reactant gas is used. This is also true in light of Seaton's experimental data (Run No. 23 and 24).

5. Thermodynamics

Several chlorination reactions are accompanied by large decreases in free energy, an extreme example being chlorination of hydrogen. Such reactions give almost complete conversion of reactants to products and the equilibrium constants are very high. For practical purposes, these reactions could be considered irreversible. In the chlorination of ethylene to form EDC, the major side reaction gives the undesirable product - trichloroethane and HCl. The desirable reaction, i.e. chlorination of ethylene to form EDC has comparatively lower decrease in free energy, but the equilibrium constant is sufficiently high, especially in the

temperature range of interest, (as shown in Table 4) so that, equilibrium conversion for this reaction, too, is almost unity.

Since trichloroethane is thermodynamically favored over EDC, successful manufacture would depend on discovery of a process and a suitable selective catalyst which speeds up the desirable reaction to the exclusion of other side reactions.

6. Reaction Mechanism

The knowledge of reaction mechanism broadens ones idea about the effects of operating conditions on the kinetics of the reaction system being investigated. It also provides a sufficient basis to tailor the experimental study to improve upon the operating conditions.

The reaction involving addition of halogen or halogen derivatives to olefinic double bond has been subject to much investigation (12,13,14). The hologenation of olefin occurs by free radical mechanism and/or ionic mechanism depending on the reaction conditions. For example, a light catalyzed and/or vapor phase reaction promotes free radical mechanism while polar mechanism is favored by ion-soluting media and the absence of light or peroxide.

There is a good experimental evidence indicating the possibility of halogen addition to olefinic double bond by free radical mechanism. The chlorine addition to tetra-chloroethylene in the vapor phase and in carbon tetrachloride

has been found to be strongly catalyzed by light and inhibited by oxygen [15]. This data could be explained by the mechanism:

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

$$Cl^{\bullet} + Cl_2C = CCl_2 \rightarrow Cl_3C - \dot{C}Cl_2$$

$$Cl_3C - \dot{C}Cl_2 + Cl_2 \rightarrow Cl_3C - CCl_3 + Cl^{\bullet} .$$

The oxygen inhibits the reaction by combining with the chain propagating radicals is evidenced by the production of trichloroacetyle chloride phosegen in this particular reaction system.

Miller and his coworkers [16] found that a mixture of oxygen, fluorine and tetrachloroethylene gives oxygenated products $Cl_2CFCOCl$, Cl_3CCOCl and $COCl_2$ in high yields in the dark at $0°C$. This points to the possibility of halogen addition by free radical mechanism even in absence of the initiator.

However, despite the frequency of halogen addition to olefinic double bond by free radical mechanism, there is good evidence supporting the possibility of this addition reaction by polar mechanism.

It was found that when bromine and ethylene are mixed in the gas phase in a glass vessel, the reaction rate decreased tenfold after coating the glass wall with paraffin. This implies much of the reaction occurs at the glass walls

of the container. The reaction rate was found to increase when the container was coated with acetyl alcohol. Also small amounts of water vapor catalyzes the reaction in the glass vessel. It could be deduced that this surface reaction involves the polar mechanism [17].

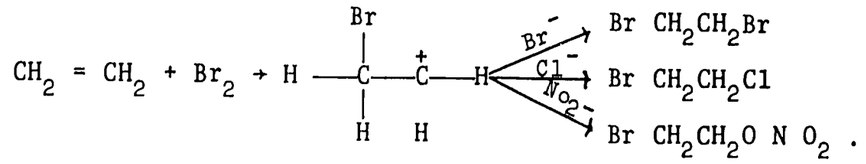
In polar mechanism, it is said that the halogen behaves as an electrophilic reagent while olefin acts as a nucleophilic reagent. The halogen molecule is said to be attracted by π electron cloud of the double bond, followed by carbon halogen-bond formation and halogen-halogen bond breaking. This results in a mono-halogenated intermediates with a positive charge.

The intermediate then reacts with the anionized part of halogen to form the adduct. The mechanism is

$$C_nH_{2n} + X - X \overset{\text{fast}}{\rightleftarrows} C_nH_{2n}.X - X \overset{\text{slow}}{\rightarrow} [C_nH_{2n}X]^+ + X^- \overset{\text{fast}}{\rightarrow} C_nH_{2n}XX .$$

Support for the assumption that the carbon-halogen bond breaking of sigma type (figure 11) takes place prior to halogen-halogen bond breaking was obtained [12] from relative reactivities of selected halogens and halogen derivatives with the same olefin in acetic acid. The relative reactivity ratios of I_2:IBγ:$B\gamma_2$:BγCl were $1:3\times10^3:10^4:4\times10^6$. This sequence stresses bond breaking as the rate controlling step, because faster rates are obtained with those halogens which depart more readily with their bonding pair of electrons.

Evidence of cationic intermediate was obtained from certain reactions between bromine and double bond in solvents like methanol, water and acetic acid. For instance, the reaction of ethylene with bromine in aqueous solution yields, in addition to ethylene bromide, some β-bromoethyl chloride in presence of sodium chloride and β bromoether nitrate in presence of sodium nitrate [13]



This addition of a bromine and a nucleophilic reagent to ethylene double bond suggests that the reaction consists of the addition of a bromine cation in the rate controlling step to yield an intermediate carbonium ion, which may rapidly react with any available nucleophilic reagent. However the exact nature of the intermediate is controversial. The two most likely forms of intermediate are shown in figure 12.

In reactions of double bond with halogens in acetic acid, the chlorination reaction was observed to be bimolecular. However reactions with bromine, iodine and iodine bromide were of higher orders, the third order often competing and dominating over second order at lower halogen concentration. The use of polar solvents, electrophiles reduced the reaction order to a bimolecular one. This could

FIG. 10. CARBON-HALOGEN BOND - FORMING OF SIGMA TYPE

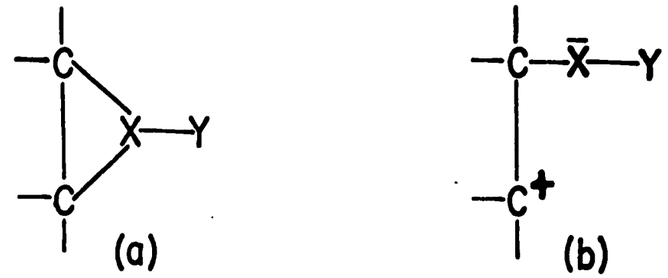


FIG. 11. POSSIBLE MOLECULAR STRUCTURE OF MONOHALOGENATED INTERMEDIATE

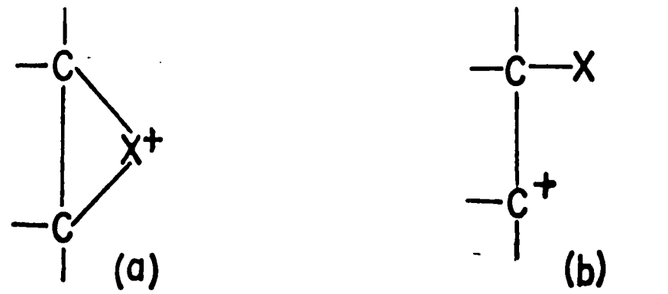
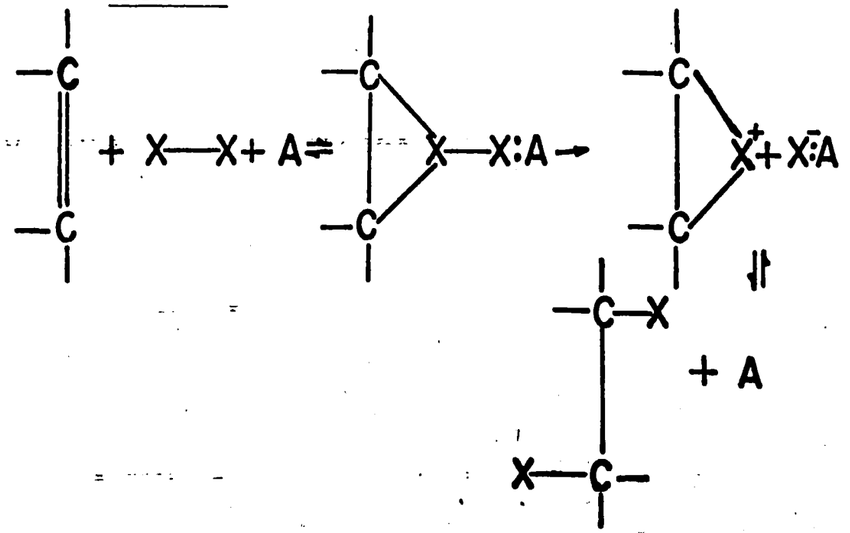


FIG. 12. REACTION MECHANISM OF HALOGENATION OF OLEFINIC DOUBLE BOND IN PRESENCE OF A WEAK ELECTROPHILIC CATALYST



be explained by the formation of trihalide ions. Anionized part of halogen molecule reacts with halogen aggregate to form trihalide ion. Electrophilic or electrolytes render the assistance of the additional halogen unnecessary by involving solvation effect on the cationic intermediate or on anionized halogen atom. The bimolecularity of chlorination is due to the ease of chlorine anionization and to the reluctance of this halogen to expand its outer valence shell.

The polar mechanism involving electrophilic attack on the olefinic double bond further explains the improvement of reaction rate when $FeCl_3$ catalyst is used. Ferric chloride is a weak electrophilic molecule. Since halogen-halogen bond breaking is the rate controlling step, the catalysis is best understood in terms of solvation of the anionized part of the halogen, expressed in figure 12. This causes reduction in free energy of activation resulting in higher reaction rates and suppression of higher order reactions. For halogen addition to most unsaturates, weak catalysis is preferrable. Strong electrophiles give rise to tendency for dehydrohalogenation. The reaction is explained in figure 13. Coordination complex formation between a halogen atom of halogenated material and the electrophile is by halogen abstraction to form a carbonium or halogenioum ion as shown in figure 13. The new halogen then reacts further with halogen to give adduct.

FIG. 13. REACTION MECHANISM OF HALOGENATION OF OLEFINIC DOUBLE BOND IN PRESENCE OF A STRONG ELECTROPHILIC CATALYST

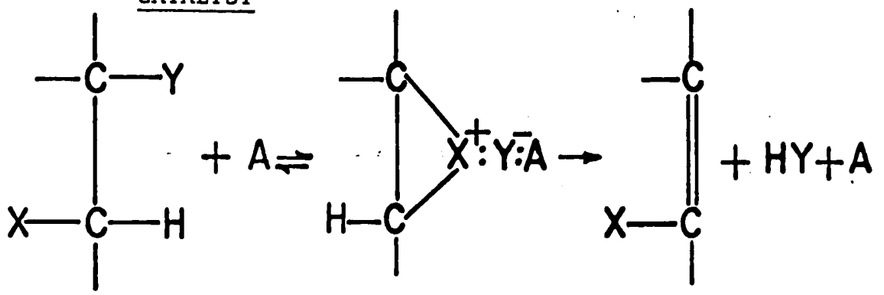
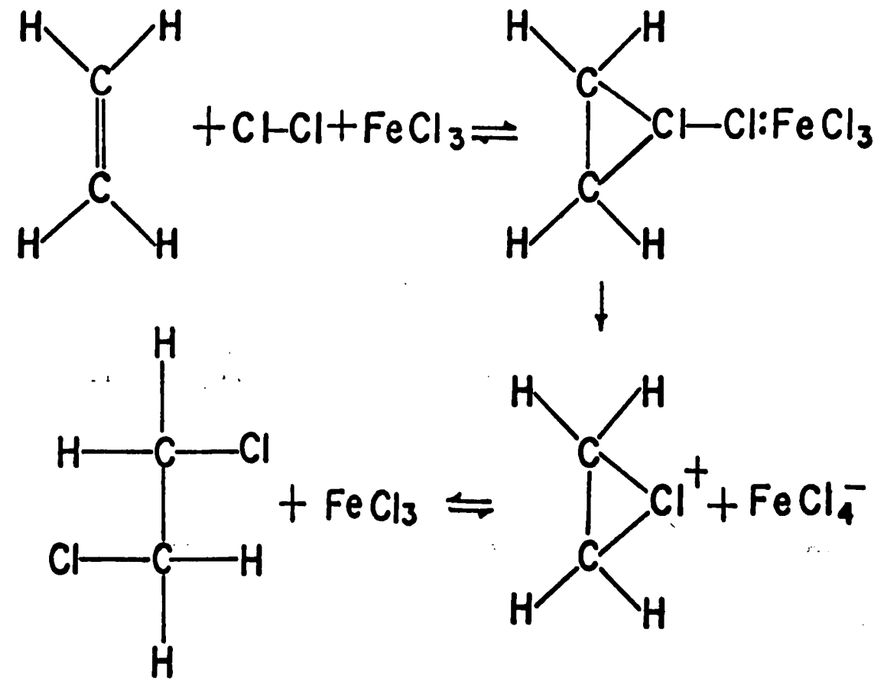


FIG. 14. REACTION MECHANISM OF CHLORINATION OF ETHYLENE IN PRESENCE OF FERRIC CHLORIDE CATALYST



The catalytic action of $FeCl_3$ in liquid-phase chlorination of ethylene is explained in figure 14. Weak electrophilic molecule $FeCl_3$ solvates with anionized halogen (chlorine) atom fascilitating the halogen-halogen (chlorine) bond breaking. This causes reduction in free energy of activation resulting in higher reaction rates and suppression of higher order reaction.

7. Catalysis

An unfortunate aspect of the reaction system under investigation is propensity to form higher chlorinated products especially at high reactor temperatures. The use of catalyst has been reported [7] mandatory not only to suppress the side reactions but to attain adequate reaction rate also. It is essential to understand the nature of catalyst action.

Galitzenstein and Woolf [19] investigated the liquid phase chlorination of ethylene for the effect of catalysts: Ferric chloride and Antimony chloride, excess of ethylene, diluted ethylene feed and temperature (4°-44°C) on substitution. They mention that substitution as high as 43% was observed when equimolar feed of ethylene and chlorine was passed through a column packed with glass pieces at temperature of 25°C. Another instance, when chlorine and ethylene were reacted in ratio of two to one at temperature of 30°-50°C in the presence of a metal catalyst such as copper, the product contained 78% trichloroethane. The substitution is

said to be induced by the addition reaction, the heat of formation of dichloroethane being utilized to form trichloroethane.

Based on this study, they suggested that substitution could be held below 2% even if no catalyst is used, if the reaction is carried out by absorbing pure ethylene while maintaining a slight excess of chlorine in the liquid phase. They observed that substitution increased substantially when a large amount of exit gas is allowed to escape by using either excess of ethylene or a diluted ethylene feed, and when no catalyst was used. The substitution could be arrested by using catalyst. Variation of temperature in the range of 4°-44°C had no influence on substitution. Careful exclusion of moisture from the reaction system was desirable to hold down substitution.

Although the literature available on homogeneous catalysis is extensive, it is inconclusive regarding the nature of catalytic action of ferric chloride.

In a recent publication, Heinmann [20] discusses the mechanisms involved in homogeneous catalysis and stresses the essential similarity of homogeneous and heterogeneous catalysis. For example, the reaction involving oxychlorination of ethylene proceeds readily in an aqueous medium with dissolved $CuCl_2$ as catalyst. It was found that presence of cuprous chloride in the solution was necessary

to attain adequate reaction rate. It was postulated the mechanism of the reaction consisted of an attack by cupric chloride on a complexed ethylene-cuprous chloride.

$$CuCl \cdot 2CuCl_2 \cdot C_2H_4 + 2CuCl_2 \rightarrow C_2H_4Cl_2 + CuCl \cdot 2CuCl_2 + 2CuCl$$

When heterogeneous catalyst, $CuCl_2$ on alumina was employed a long induction time was observed. However when heterogeneous catalyst, $CuCl \cdot 2CuCl_2$ on alumina was used as a catalyst, the results were comparable to that of homogeneous catalysis. In view of these experimental results, it appears that there must be a slow direct reaction of gaseous ethylene with solid $CuCl_2$ to create cuprous chloride which then complexes with ethylene and makes it more readily available to attack by cupric chloride. The author compares the cupric-cuprous chloride catalytic action similar to enzymatic catalytic action, which is said to be due to enzyme's ability not only to attract the reactant atoms but to steer their orbitals along a path that takes advantage of this directional preference.

Based on Sebatier's [22] findings, it is very doubtful that ethylene receives chlorine from $FeCl_3$, leaving ferrous chloride which then reacts with chlorine to regenerate ferric chloride. He reports that when a large excess of benzene was contacted with ferric chloride and kept at 40°C for 30 hours, reduction of $FeCl_3$ by benzene was very slight, when dry chlorine was bubbled through the mixture, despite

extensive chlorination, very small amount of ferrous chloride was detected.

As discussed earlier, the catalytic action of $FeCl_3$ might be due to solvation of the anionized halogen atom, resulting in decrease in free energies of activation. This means lower reaction order and higher reaction rate. Reaction orders are reduced because the presence of an electrophilic agent renders the assistance of additional halogen molecule unnecessary.

Another possibility is increase in the total interfacial area when the catalyst is added. Calderbank [4] mentions "when a small quantity of one of a number of hydrophylic solutes was added to water, the interfacial area was found to be increased by a large factor. The solutes are present in too small an amount to effect the interfacial tension to a measurable extent. However, the presence of solutes exerts a profound effect on the ease with which gas bubbles coalesce. With water containing a small amount of alcohol, no coalescence is observed. The dynamic behavior set up between the dispersion and coalescence in aerated mixture is upset by the presence of many solutes."

Still another possibility is an increase in the solubility of ethylene and chlorine due to ferric chloride-ethylene and/or ferric chloride-chloride complex formation. This would increase the mass transfer driving force at the boundaries

of the ethylene liquid film. This means higher conversion and yield of ethylene.

On detailed calculation, it was found that the molar concentration of ferric chloride is too small compared to the molar concentrations of reactant gases in the liquid film to significantly alter the reaction rate.

Seaton found no improvement in reaction rate with increase in catalyst concentration. Normally, if the interfacial area was increased by catalyst presence due to suppression of bubble coalescence, the reactor performance should improve with increase in catalyst concentration. This indicates that it is unlikely that catalyst presence results in an increase of interfacial area due to inhibition of bubble coalescence.

This means the assumption that reaction rate is instantaneous is not valid especially at higher temperature when mass transfer driving forces are relatively small. The catalyst presence speeds up the desirable reaction to the suppression of others.

VI. VAPOR-LIQUID EQUILIBRIUM DATA

1. Ethylene Solubility Data

The available data on ethylene solubility in EDC is scarce and inconsistent within itself. Seidell [25] reported Henry's law constant of 5000 atm - cc/g mole for ethylene solubility in EDC at 0°C and 1 atm. However the Henry's law constant for ethylene in EDC as reported by Balasubramanian et al. is 32,700 atm cc/g mole at 32°C and 1 atm. Seven fold increase in Henry's law constant with temperature rise of 32°C is very unlikely.

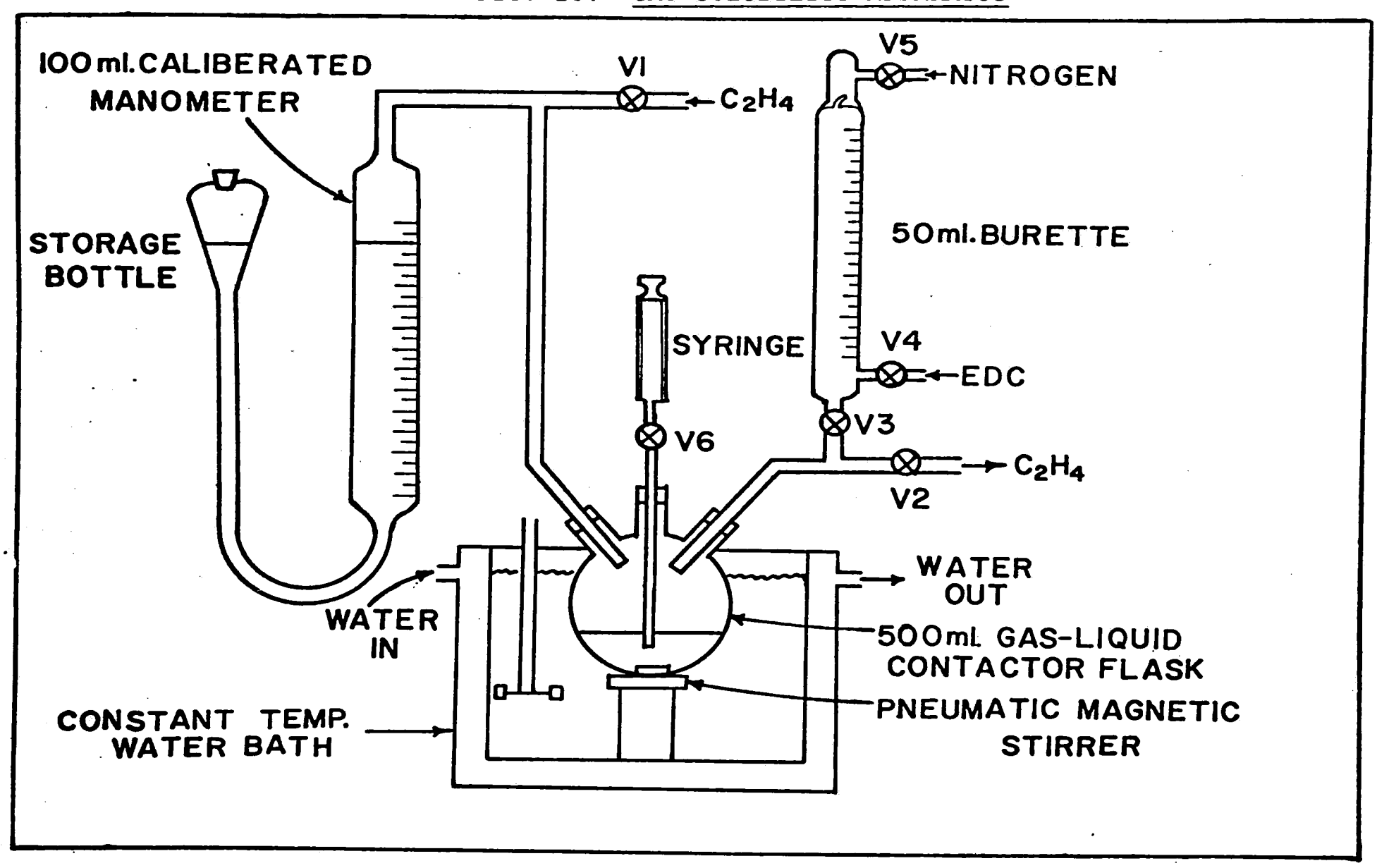
Apparatus and Procedure

To generate vapor liquid equilibrium data for ethylene-EDC system, the apparatus shown in figure 15 was used. The apparatus is based on the principle similar to that of Orsat's apparatus used in fuel gas analysis. The solubility of ethylene in EDC was experimentally obtained at temperatures 32°C and 50°C with/without catalyst.

The gas liquid contactor is a 500 ml flask immersed in a constant temperature water bath equipped with a stirrer and automatic temperature controller.

Initially the system was purged with ethylene to remove the air originally present. The ethylene inlet valve V1 and exit valve V2 were opened, keeping all other valves closed. Special care was taken to prevent air leakage in the system.

FIG. 15. GAS SOLUBILITY APPARATUS



When valves V1 and V2 were closed, a fixed amount of ethylene was trapped in the system. Since the gas-liquid contactor flask was immersed in water bath at desired experimental temperature, the ethylene gas would attain the experimental temperature gradually. This is evidenced by stabilization of the mercury level in the manometer arm. At this stage, the initial volume and pressure of the system were recorded (Vi, Pi).

If T is the desired experimental temperature then the total number of moles of ethylene trapped is:

$$n_1 = Pi \times Vi/R \times T \ .$$

After the ethylene gas had attained the experimental temperature, 100 ml of EDC was introduced in the gas-liquid contactor flask via the burrette to fascilitate EDC transfer to the flask and to prevent ethylene escape through the burrette. EDC in the flask was stirred with a pneumatic magnetic stirrer to improve gas-liquid contact.

Control of the system pressure was possible by moving the mercury storage bottle up and down. When the storage bottle moves down, the mercury level in the 100 ml manometer arm (caliberated) dropped, thereby, increasing the total volume of the system. This results into a decrease in system pressure. The mercury level in the manometer arm would stabilize when the system had attained the experimental temperature and the ethylene dissolving in EDC had stopped.

At this stage the final pressure and volume of the system were noted (P_f, V_f) .

$$\text{Volume of the gas phase} = V_f - \text{volume of EDC}$$
$$= V_f - 100$$
$$\text{Partial pressure of ethylene} = (P_f - P_{EDC})$$

where P_{EDC} = partial pressure of EDC equal to EDC vapor pressure at the experimental temperature.

Total moles of ethylene present at the end = n_2

$$= \frac{(V_f - 100)(P_f - P_{EDC})}{R \times T}$$

Moles of ethylene dissolved in 100 ml of EDC = $n_1 - n_2$

$$\text{Henry's law constant} = \frac{\text{Pethylene}}{\frac{n_1 - n_2}{100}} \quad \frac{\text{atm cc}}{\text{g-mole}}$$

$$= \frac{(P_f - P_{EDC}) \times 100}{(n_1 - n_2)} \quad \frac{\text{atm cc}}{\text{gm mole}} \qquad (13)$$

P_f and P_{EDC} are in atmospheres.

To provide a check on the ethylene solubility in EDC determined by the previous method, provision was made to withdraw a sample of 15 cc from the flask with a syringe and to estimate ethylene concentration in the sample chemically.

The sample was titrated idometrically using Bromide-Bromate method to estimate ethylene concentration.

10 ml of distilled water was placed in a bromination

bottle (figure 16). The bottle was stopped and evacuated to 1/3 atm pressure or lower. The 15 ml sample from the syringe was transferred to the evacuated bottle by inserting the tip of the syringe into a short piece of rubber tubing connected to the stopcock of the bottle stopper and opening the stopcock to an extent sufficient to draw the liquid from the syringe at its normal drainage rate. When the sample was drained, the stopcock was closed. The syringe was withdrawn, the tubing and the stopcock were flushed with 10 ml of acetic acid.

Next 30 ml of 0.2 N bromide-bromate reagent was added. Immediately 30 ml of 10% sulfuric acid was introduced. The bottle was shielded from strong light and shaken for 5 minutes.

The reaction was stopped by drawing 15 ml of 20% potassium iodide solution into the bottle, following by 100 ml of distilled water. The liberated iodine was immediately titrated with a 0.1 N Standard sodium thiosulfate solution using starch indicator solution.

$$\text{Moles of bromine liberated} = \frac{V \times N}{1000} = \frac{30 \times 0.2}{1000} = 6 \times 10^{-3}$$

$$\text{Moles of bromine reacted with sodium thiosulphate} = \frac{v \times n}{1000} = \frac{v \times 0.1}{1000}$$

$$= v \times 10^{-4}$$

$$\text{Moles of bromine reacted with ethylene} = 6 \times 10^{-3} - v \times 10^{-4}$$

Considering that 2 atoms of bromine react with an ethylene molecules,

$$\text{Moles of ethylene present in the sample} = \frac{6\times10^{-3}-v\times10^{-4}}{2}$$

$$\text{Henry's law constant} = \frac{P_f - P_{EDC}}{\frac{6\times10^{-3}-v\times10^{-4}}{2\times15}} = \frac{30(P_f - P_{ED})}{6\times10^{-3}-v\times10^{-4}} \quad (14)$$

To investigate effect of catalyst presence on EDC solubility, a saturated solution of ferric chloride in EDC was used. It was prepared by contacting excess of ferric chloride with EDC under nitrogen atmosphere.

RESULTS AND CONCLUSIONS

The results of the experiments are shown in Table 4. The Henry's law constant obtained from equation (14) was considered more accurate.

To approximate ethylene solubility in EDC at various temperatures, Henry's law constant was assumed to vary linearly with temperature.

Figure 16 shows a plot of Henry's law constant for ethylene in EDC versus temperature.

2. Chlorine Solubility in EDC

To estimate chlorine solubility in EDC, Shair's correlation (equation (8), (5), (6) in reference [27]) was used. It states:

Considering that 2 atoms of bromine react with an ethylene molecules,

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2. Chlorine Solubility in EDC

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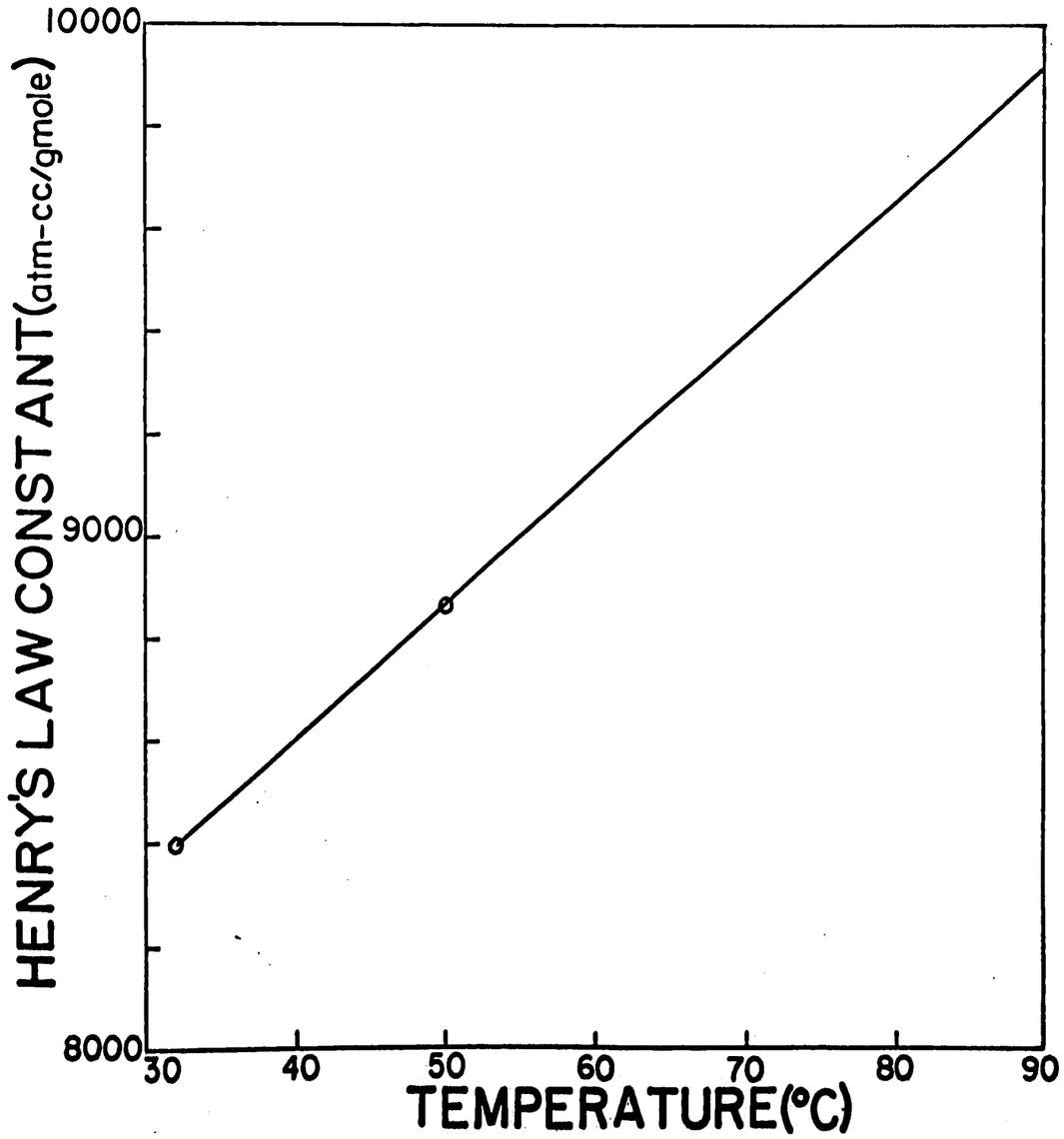
TABLE 4

Sample Number	Temp °C	Catalyst cncnt.	V_i cc	P_i mm% Hg	V_f cc	P_f mm% Hg	P_{EDC} mm% Hg	v-volume of 0.1 N $Na_2C_2O_3$ used in tritration	H_E from Eq.13	H_E from Eq.14
1	32	0.0	700	750	640	750	117	30.0	8644	8404
2	32	saturated solution	700	750	632	750	117	30.0	8422	8404
3	50	0.0	606	750	589	750	237	37.0	8807	8868
4	50	saturated solution	600	750	578	750	237	36.8	8768	8800

FIG. 16. EFFECT OF TEMPERATURE ON ETHYLENE SOLUBILITY IN EDC



$$\frac{1}{X_c} = \frac{f_c^{\,L}}{f_c^{\,G}} \; EXP \left\{ \frac{v_c^{\,L}(\delta_{EDC}-\delta_L)^2 \; \phi_{EDC}^2}{R \times T} \right\} \qquad (1)$$

At low pressures and low molar concentrations

$$f_c = P_c \qquad (2)$$

$$H_c = P_c/X_c/v_{ED} = \frac{P_c(v_{EDC})}{X_c} \qquad (3)$$

Combining equations (1), (2) and (3):

$$H_c = f_c^{\,L} \cdot v_{EDC} \cdot EXP \left\{ \frac{v_c^{\,L} \cdot (\delta_{EDC}-\delta_c)^2 \cdot \phi_{EDC}^2}{R \cdot T} \right\} \qquad (4)$$

$f_c^{\,L}$=0.1+EXP{4.95(T/416-.715)} 76.1 [Figures 8 and 9, [27]]

δ_{ED} = 10.2

δ_c = 8.7

ϕ_{EDC}= 1.0

$v_c^{\,L}$ = 76.0

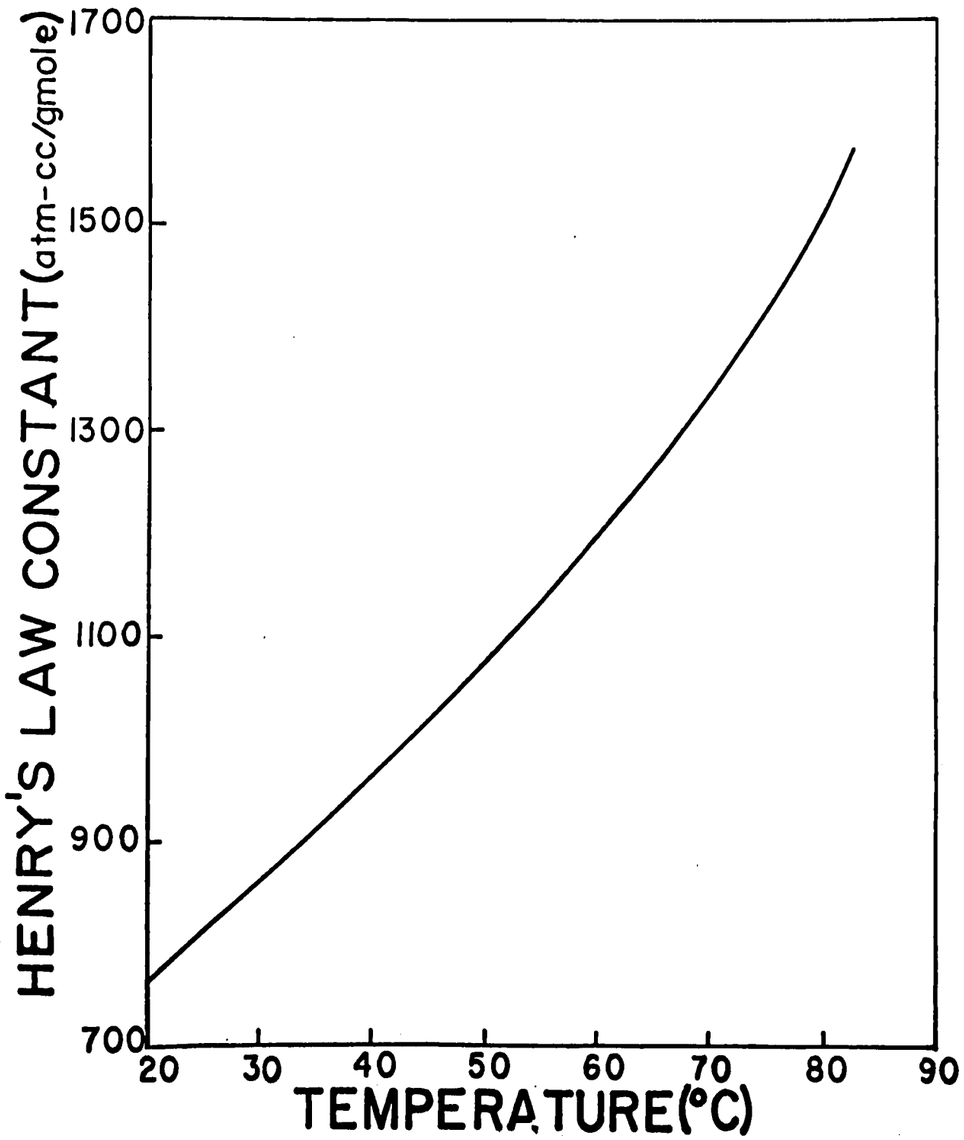
v_{ED} = 79.5

Substituting the values of the constants in equation (4):

$$H_c = \{0.1 + EXP\ (4.95[T/416-.715])\} \cdot 79.5 \cdot 76.1 \cdot EXP \left\{ \frac{74.0(1.5)^2}{RT} \right\} \qquad (5)$$

A plot of Hc versus T (Henry's law constant for chlorine in EDC versus temperatures) based on equation (5) as given in figure 17.

FIG. 17. EFFECT OF TEMPERATURE ON CHLORINE SOLUBILITY IN EDC



The effect of catalyst presence on chlorine solubility would be too small in most cases even if ferric chloride forms complex with chlorine. The ferric chloride concentration of 2 gms/ℓ in EDC is equivalent to 10^{-3} mole fraction of ferric chloride in EDC.

Compared to that chlorine solubility is 0.1 mole/mole of EDC at 1 atm total pressure and 32°C. Even if one or two molecules of chlorine combine with ferric chloride to form the complex, the resultant increase in solubility would be too small to effect the reactor performance and too difficult to determine experimentally.

VI. MASS AND ENERGY BALANCE - A SIMPLE MODEL

Consider a simplified reactor operation when ethylene and chlorine are bubbled separately in EDC. Assume no undesirable side reactions occur. (C'=Y'). The unreacted reactant gases escape to the atmosphere (no condenser). The atmospheric heat losses are negligible. The process is depicted in figure 18.

Flow rate of unreacted ethylene = $F_E(1-C')$

Flow rate of unreacted chlorine = $F_C - F_E \times C'$

Flow rate of unreacted gases leaving the reactor

$$= F_C + F_E(1-2C')$$

EDC vapor flow rate leaving the reactor

$$= \frac{P_{ED}'}{(P-P_{ED}')} \times \{F_C+F_E(1-2C')\} \quad (15)$$

The rate of heat generation due to reaction

$$= F_E \times C' \times H_R \quad (16)$$

The rate of heat generation due to reaction would be equal to the rate of heat used to vaporize EDC at steady state.

H_R is the exothermic heat of reaction. The rate of heat consumption to vaporize EDC

$$= (\Delta H)_{ED} \times \frac{P_{ED}'}{(P-P_{ED}')} \times \{F_C+F_E(1-2C')\} \quad (17)$$

Considering that the heat generated due to the reaction is used to evaporate EDC, from Eq. (16) and Eq. (17)

$$F_E \times C' \times H_R = \Delta H_{ED} \times \frac{P_{ED}'}{(P-P_{ED}')} \times \{F_C+F_E(1-2C')\}$$

Simplifying,

$$P_{ED}' = \frac{C' \times H_R \times P}{C' \times H_R + \Delta H_{ED} \times \{\frac{F_C}{F_E}+1-2C'\}} \qquad (18)$$

$$P_{ED}' = e^{A+B/T+x}$$

where A, B and x are constants and T is the auto-refrigeration operating temperature.

$$T = - x + \frac{B}{(\ell n P_{ED}' - A)} \qquad (19)$$

Figure 19 shows plots of autorefrigeration equilibrium temperature versus conversion of ethylene for the three operating pressures 170 mm, 380 mm and 760 mm. They are based on Eq. (18) and Eq. (19).

Except for the autorefrigerated runs at 170 mm pressure, the equilibrium operating temperatures of the autorefrigerated runs show very little deviation from the autorefrigeration equilibrium temperature predicted by Eq. (18) and Eq. (19). The anomaly observed with autorefrigerated runs at 2/9 atm. could be due to the EDC vapor loss via condenses (higher at low pressure).

FIG. 18. MODEL REPRESENTATION OF REACTOR OPERATION WHEN NO SIDE-REACTION OCCURS

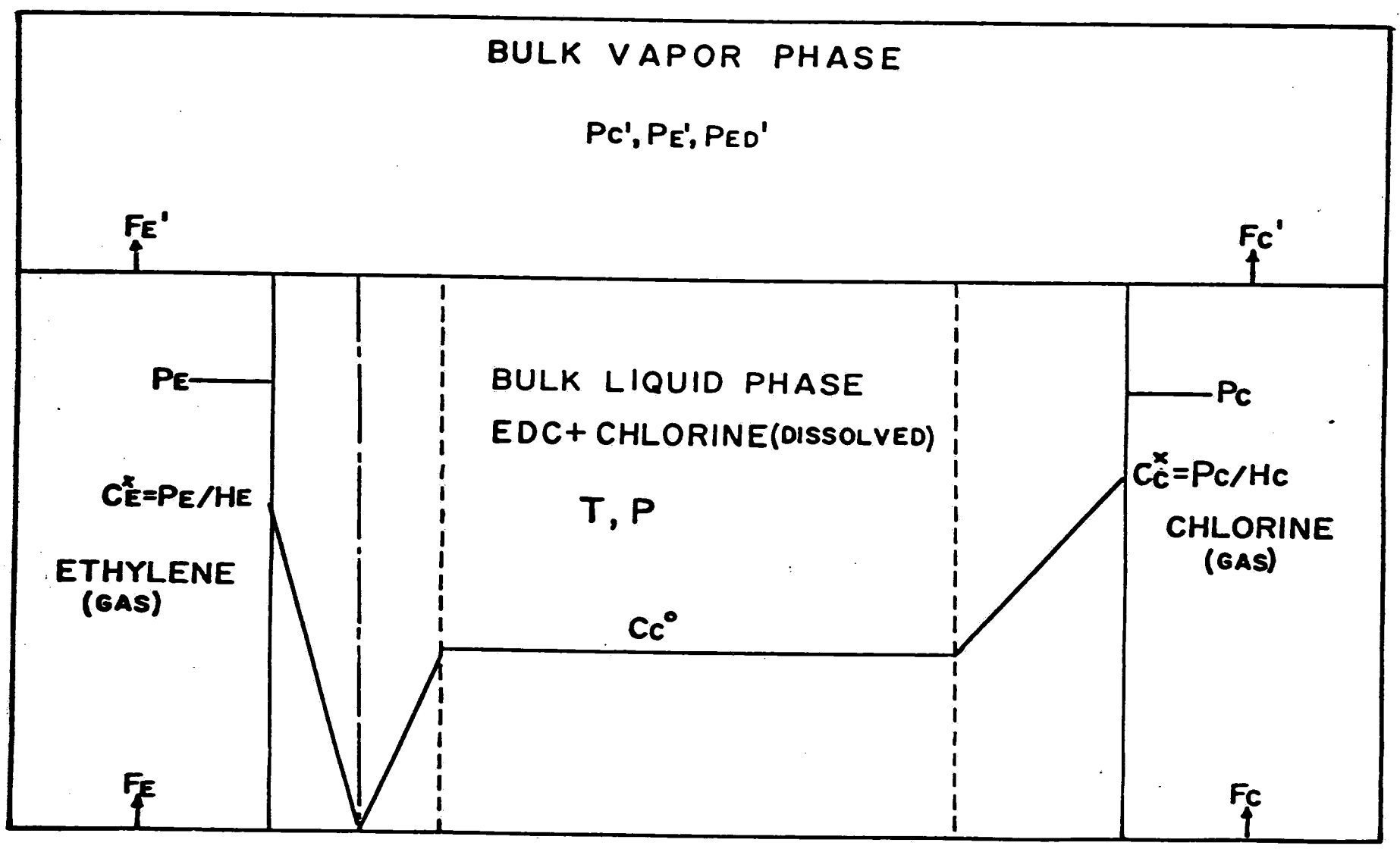
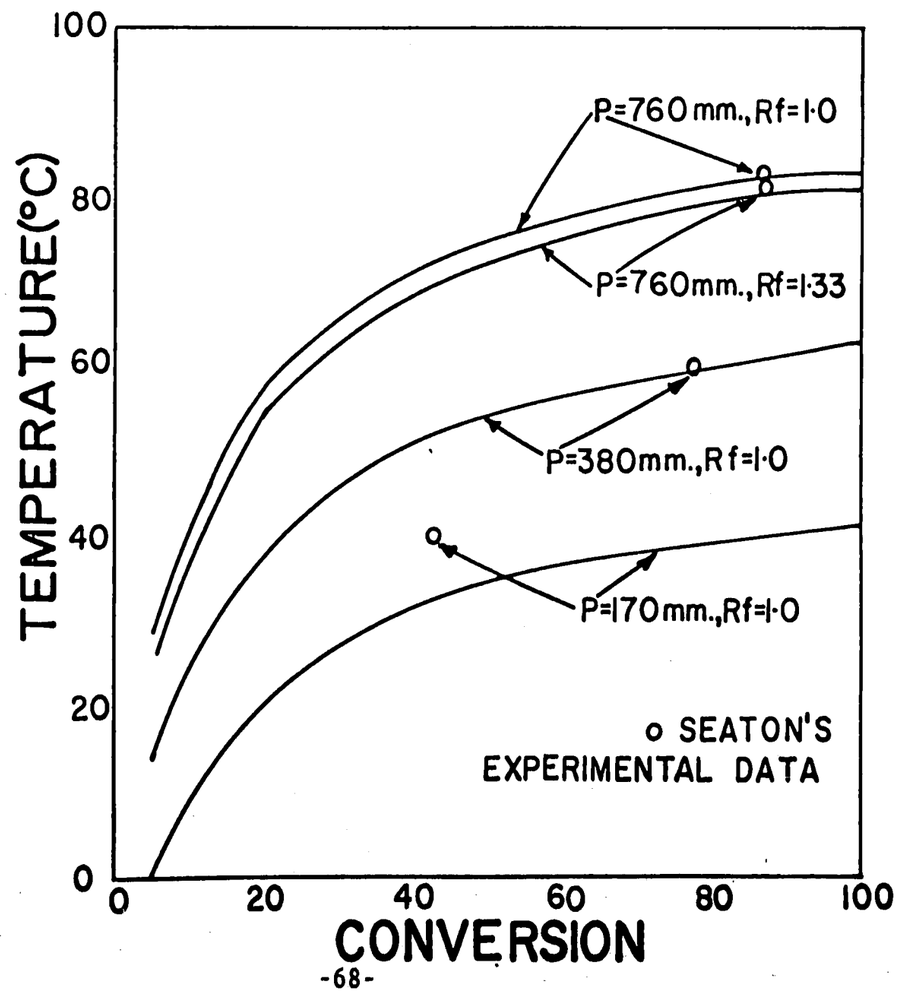


FIG. 19. EFFECT OF CONVERSION OF ETHYLENE ON AUTOREFRIGERATED REACTOR EQUILIBRIUM TEMPERATURE (SIMPLIFIED REACTOR MODEL)



VII. MASS AND ENERGY BALANCE - A MORE RIGOROUS MODEL

The pictorial representation of the mathematical model for the reactor system is depicted in figure 20 and figure 21.

The term used in the figures are explained in appendix E.

This model is based on the following assumptions.

1) No reaction takes place in the vapor phase in the reactor.
2) No reaction occurs in the vapor phase or liquid phase in the condenser.
3) HCl evolved due to substitution reaction does not diffuse to the reactant gas bubbles.
4) The reaction between ethylene and chlorine is fast enough to be considered instantaneous.
5) The mass transfer resistance in the reactant gas bubble is negligible and the liquid phase resistance can be adequately represented by liquid film model.
6) Bubble coalescence is negligible.
7) The chlorine concentration in the liquid phase in the reactor is related to chlorine partial pressure in the bulk vapor phase by Henry's law. The same holds true in condenser.
8) The reaction due to absorption of ethylene from the bulk vapor phase to the bulk liquid phase is negligible.

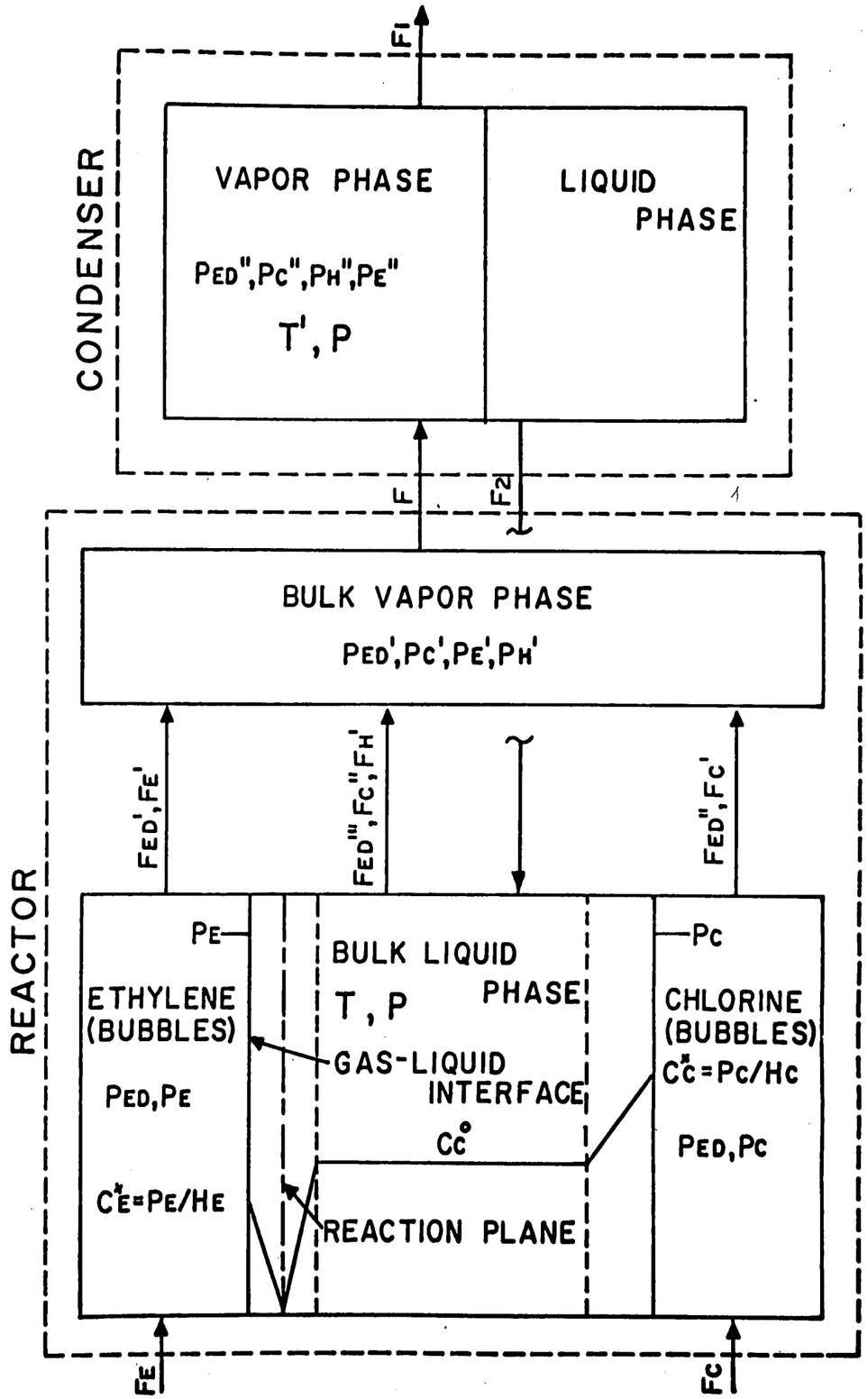


FIG. 20. MODEL REPRESENTATION OF REACTOR SYSTEM

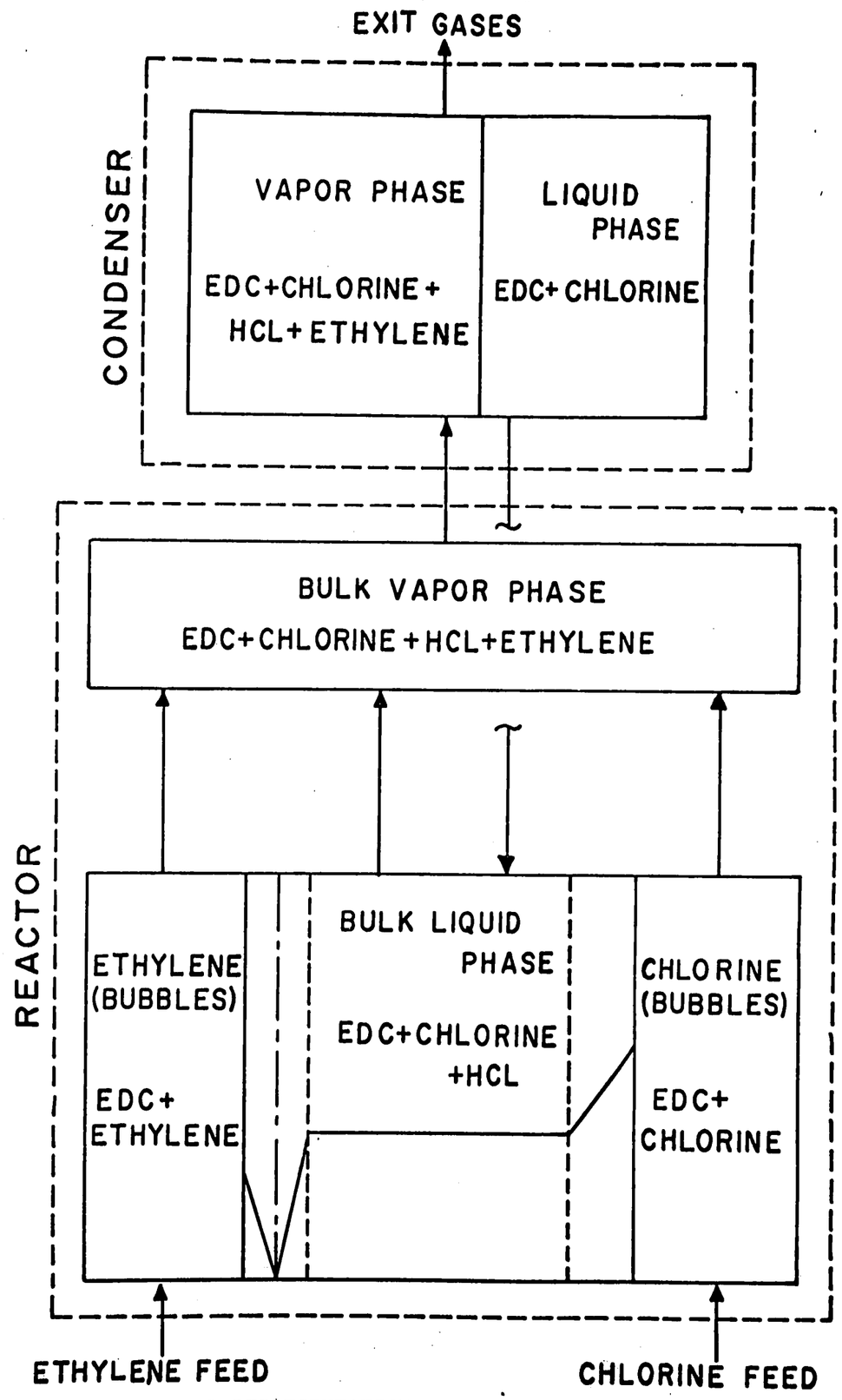


FIG. 21. MODEL REPRESENTATION OF REACTOR SYSTEM

9) The EDC evaporation into reactant gas feed bubbles is accomplished in such a short time that it could be considered instantaneous.

10) The heat of solution of reactant gases is negligible.

Material Balance for the Reactor

If C' and Y' are actual conversion and yield of ethylene, then

Overall continuity equation:

$$F = F_E' + F_C' + F_C'' + F_H' + F_{ED}' + F_{ED}'' + F_{ED}'' \quad (19.1)$$

Component continuity equations:

Ethylene:

$$F_E' = (1-C')F_E = \frac{P_E'}{P} \times F \quad (20)$$

Chlorine:

$$F_C' + F_C'' = F_C + F_2 x_C' - (2c'-y')F_E \quad (21)$$

$$F_C' + F_C'' = \frac{P_C'}{P} \times F \quad (22)$$

Hydrogen chloride:

$$F_H' = \frac{P_H'}{P} \times F = (C'-Y')F_E \quad (23)$$

EDC:

$$\frac{P_{ED}'}{P} \times F = F_{ED}' + F_{ED}'' + F_{ED}''' \quad (24)$$

Material Balance for the Condenser

Overall continuity equation:

$$F = F_2 + F_1 \quad (25)$$

Component continuity equations:

Ethylene:

$$\frac{P_E'}{P} \times F = \frac{P_E''}{P} \times F_1 \qquad (26)$$

Chlorine:

$$\frac{P_C'}{P} \times F = \frac{P_C''}{P} \times F_1 + x_C' \times F_2 \qquad (27)$$

Hydrogen chloride:

$$\frac{P_H'}{P} \times F = \frac{P_H''}{P} \times F_1 \qquad (28)$$

EDC:

$$\frac{P_{ED}'}{P} \times F = \frac{P_{ED}''}{P} \times F_1 + F_2(1-x_C') \qquad (29)$$

If x_C' is assumed to be equal to C_C' at low molar concentrations of chlorine in EDC

$$H_C' = \frac{P_C'' \times v_{ED}}{C_C'} = \frac{P_C'' \times v_{ED}}{x_C'} \qquad (30)$$

where H_C' is Henry's law constant at the condenser reflux temperature.

From Eq. (30)

$$P_C'' = H_C' \, x_C' / v_{ED}$$

From Eq. (25)

$$F_2 = F - F_1 \qquad (31)$$

substituting for F_2 from Eq. (31) in Eq. (29)

$$x_C' = \left\{ \frac{P_{ED}''}{P} \times a + (1-a) - \frac{P_{ED}'}{P} \right\} \Big/ (1-a) \qquad (32)$$

where $a = F_1/F$.

Substituting for F_2 from Eq. (31) and for P_C'' from Eq. (30) in Eq. (27)

$$\frac{P_C'}{P} = \frac{H_C' \, x_C' \times a}{v_{ED} \times P} + x_C'(1-a) \quad . \tag{33}$$

Combining Eq. (32) and Eq. (33)

$$\frac{P_C'}{P} = \frac{\left(\frac{H_C' \times a}{v_{ED} \times P} + 1 - a\right)\left(\frac{P_{ED}''}{P} \times a + (1-a) - \frac{P_{ED}'}{P}\right)}{(1-a)} \quad . \tag{34}$$

Combining Eq. (19.1), Eq. (32), Eq. (20), Eq. (21), Eq. (24) and Eq. (23)

$$F = (1-C')F_E + \left[F_C + \left\{\frac{P_{ED}''}{P} \times a + (1-a) - \frac{P_{ED}'}{P}\right\} \times F - (2C'-Y')F_E\right] + (C'-Y')F_E + \frac{P_{ED}'}{P} \times F \tag{35}$$

Simplifying Eq. (35)

$$F = \frac{F_C + F_E(1-2C')}{\left[1 - \left\{\frac{P_{ED}''}{P} \times a + (1-a) - \frac{P_{ED}'}{P}\right\} - \frac{P_{ED}'}{P}\right]} \tag{36}$$

Combining Eq. (21), Eq. (22) and Eq. (32)

$$\frac{P_C'}{P} = \frac{F_C' + F_C''}{F} = \frac{F_C + \left\{\frac{P_{ED}''}{P} \times a + 1 - a - \frac{P_{ED}'}{P}\right\} F - (2C'-Y')F_E}{F} \tag{37}$$

Energy Balance for Reactor

If the atmospheric heat losses are considered negligible, then the heat generated due to reactions would be equal to the heat used in EDC vaporization plus heat used

in heating up of the inlet streams in autorefrigerated runs.

$$\text{Heat generated in the reactor} = \{\Delta H_R Y' + \Delta H_C (C'-Y')\}F_E \tag{38}$$

where ΔH_R - exothermic heat of reaction between chlorine and ethylene to form EDC at the reactor temperature.

ΔH_C - exothermic heat of substitution reaction at reaction temperature.

Heat used in EDC evaporation

$$= \Delta H_V (F_{ED}' + F_{ED}'' + F_{ED}'')$$

$$= \frac{H_V \cdot F \cdot P_{ED}'}{P} \tag{39}$$

Heat used in heating up of the inlet streams to the reactor temperature

$$= (CP_E \cdot F_E + CP_C \cdot F_C)(T-298.) + CP_{ED} \cdot F_2 (T-T')$$

$$= (CP_E \cdot F_E + CP_C \cdot F_C)(T-298.) + CP_{ED} \cdot (1-a)F(T-T') \tag{40}$$

The heat capacity of the reflux stream is assumed to be equal to the heat capacity of EDC.

From Eq. (38), Eq. (39), Eq. (40)

$$(\Delta H_R Y' + \Delta H_C C')F_E = \Delta H_V \cdot F \cdot P_{ED}' + (CP_E \cdot F_E + CP_C \cdot F_C)(T-298.) + CP_{ED} \cdot (1-a)F \cdot (T-T') \tag{41}$$

If T, P, F_E and F_C are known, then Eq. (41) could be written as

$$f_1(Y',C',F,P_{ED}',a,T') = 0 \qquad (42)$$

Since $P_{ED}' = f(T)$, Eq. (42) could be simplified to

$$f_1(Y',C',F,a,T') = 0 \qquad (43)$$

Similarly Eq. (37) is reduced to the form

$$f_2(P_C',F,P_{ED}'',P_{ED}',a,C',Y') = 0 \qquad (44)$$

Since $P_{ED}' = f(T)$ and $P_{ED}'' = f(T')$, Eq. (44) could be simplified to

$$f_2(P_C',F,T',a,C',Y') = 0 \qquad (45)$$

Similarly Eq. (36) is reduced to the form

$$f_3(F,C',T',a) = 0 \qquad (46)$$

Similarly Eq. (34) is reduced to the form

$$f_4(P_C',a,T') = 0 \qquad (47)$$

There are six variables and four independent equations. The system has two degrees of freedom. If the values of any two variables out of these six variables are known, the values of the other four variables are fixed. This holds good for the autorefrigerated reactor only.

If the operating conditions (F_E, F_C, P, T) are known for an autorefrigerated reactor, then for a specified value of T' (condenser exit gas temperature) there corresponds only one value of C' (conversion of ethylene) for a given value of Y' (yield of ethylene). The temperature of the cold water being circulated in the condenser was 8-10°C. The exit gas temperature would be most likely in the temperature range of 10°C to 20°C. The curves representing feasible sets of values of (C',Y') were obtained at various T' in the range of 10-30°C for the operating conditions observed in the autorefrigerated experimental runs. There are three more restrains on the feasible sets of values (C',Y') could take. The conversion of chlorine and ethylene can not exceed 100% and conversion of ethylene can not be lower than yield of ethylene.

$$2C' - Y' \leq F_C/F_E, \quad C' \geq Y', \quad Y' \leq 100$$

It was found that T' (condenser exit gas temperature) and reactant feed rates had very slight effect on the feasible sets of values of (C',Y').

The feasible set of values of (C',Y') was mainly influenced by ΔT, the difference between reactor temperature and EDC boiling point at the reactor pressure and the feed ratio. Figure 22 represents feasible set of

FIG. 22. POSSIBLE SET OF VALUES OF CONVERSION AND YIELD OF ETHYLENE FOR AUTOREFRIGERATED REACTOR OPERATION AT (2/9 atm. and 40°C), (1/2 atm. and 60°C) AND (1 atm. and 82.5°C)

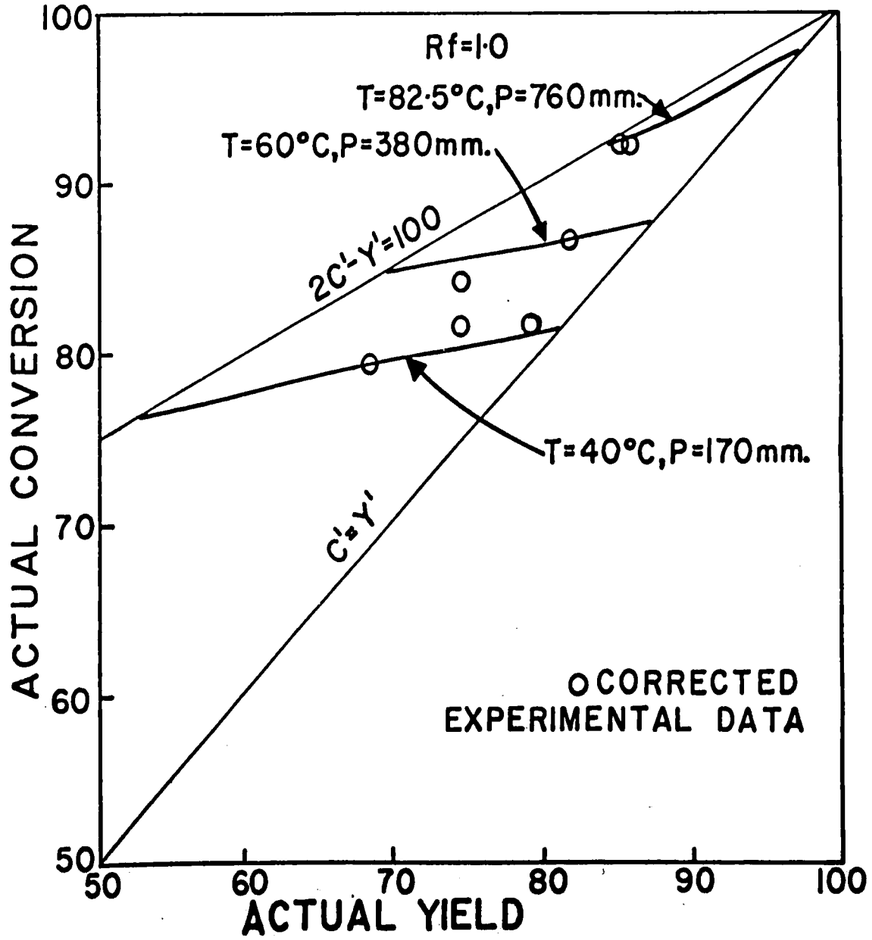
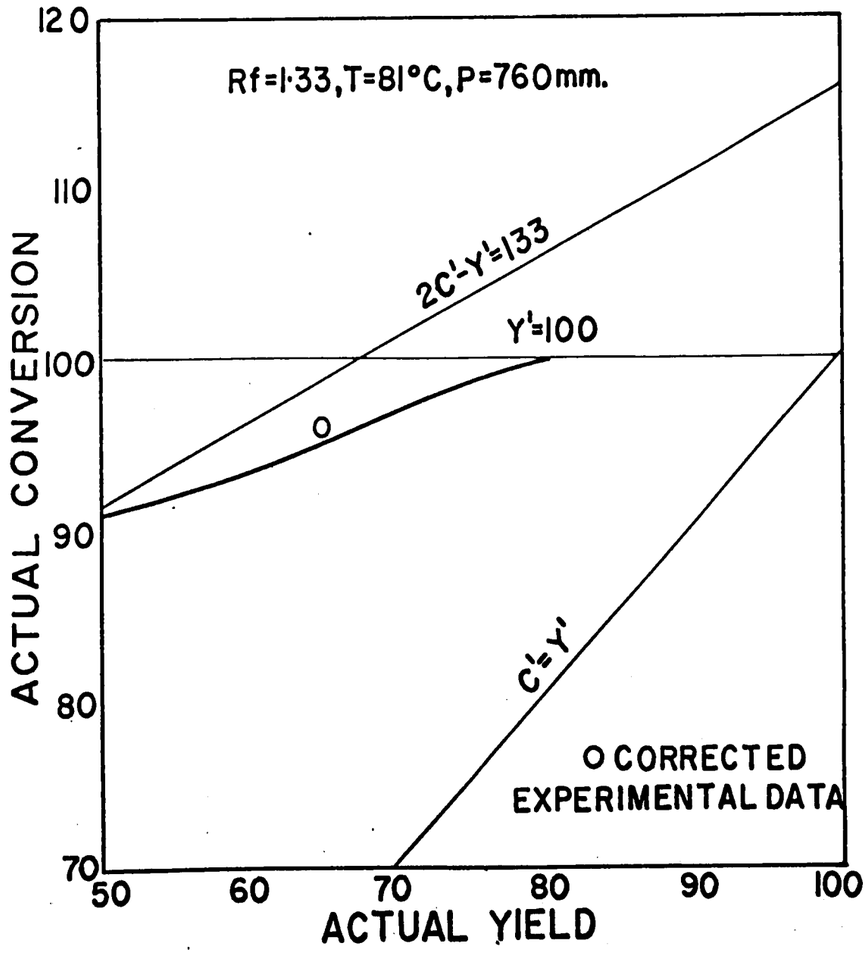


FIG. 23. POSSIBLE SET OF VALUES OF CONVERSION AND YIELD OF ETHYLENE FOR AUTOREFRIGERATED REACTOR OPERATION AT (1 atm., 81°C and R_f=1.33)



values of (C',Y') for operating conditions (R_f=1.0, T=40°C, P=.222 atm), (R_f=1.0, T=60°C, P=0.5 atm) and (R_f=1.0, T=82.5°C, P=1 atm). Figure 23 represents feasible set of values of (C',Y') for operating conditions (R_f=1.33, T=81°C, P=1 atm).

As discussed earlier, the autorefrigerated reactor system has two degrees of freedom for a given set of operating conditions (F_C,F_E,P,T). If the actual conversion and yield of ethylene are known, the reactor system is completely defined. However, the observed conversion and yield of ethylene are known for the autorefrigerated runs.

The actual conversion and yield of ethylene were approximated from the observed conversion and yield of ethylene by trial and error method. As an initial approximation, the actual conversion and yield of ethylene were assumed to be equal to the observed conversion and yield of ethylene. Then Eq. (43), Eq. (45), Eq. (46) and Eq. (47) were solved for the values of P_C', F, T' and a . The molar flow rate of EDC vapor from condenser = F_{ED}'' = $\frac{P_{ED}''}{P} \times F_2 = \frac{P_{ED}''}{P} \times a \times F$. As the next approximation, the actual conversion and yield of ethylene were assumed to be equal to the observed conversion of ethylene plus F_{ED}''/F_E and observed yield of ethylene plus F_{ED}''/F_E respectively. This was repeated until two consecutive approximated values of actual conversion and yield of

ethylene differed by less than 0.3 percent.

In case of conventionally cooled reactor, Eq. (41) representing reactor energy balance for adiabatic operation is no longer valid. There is one less restrain on conventionally cooled reactor compared to autorefrigerated reactor. Hence a conventionally cooled reactor has three degrees of freedom. Knowledge of the three variables is necessary to define the system. Observed conversion and yield of ethylene being known, the condenser exit gas temperature was assumed to be 12°C, 13°C and 34°C in the reactor temperature range of 30-45°C, 45-65°C and 65-80°C respectively. For a given condenser exit gas temperature, the actual conversion and yield of ethylene was obtained from observed conversion and yield of ethylene by trial and error method using Eq. (45), Eq. (46) and Eq. (47).

Table 4 shows the condenser temperature and corrected conversion and yield data for Seaton's experimental runs. (The experimental results which showed inconsistency on mass and energy balance of the reactor system were eliminated.) Figure 24, figure 25, figure 26 and figure 27 compared the observed experimental data and the corrected experimental data.

Table 7 represents a detailed heat balance for the reactor and the condenser.

FIG. 24. EFFECT OF TEMPERATURE ON CORRECTED CONVERSION OF ETHYLENE FOR CONVENTIONALLY COOLED REACTOR WITH AND WITHOUT CATALYST

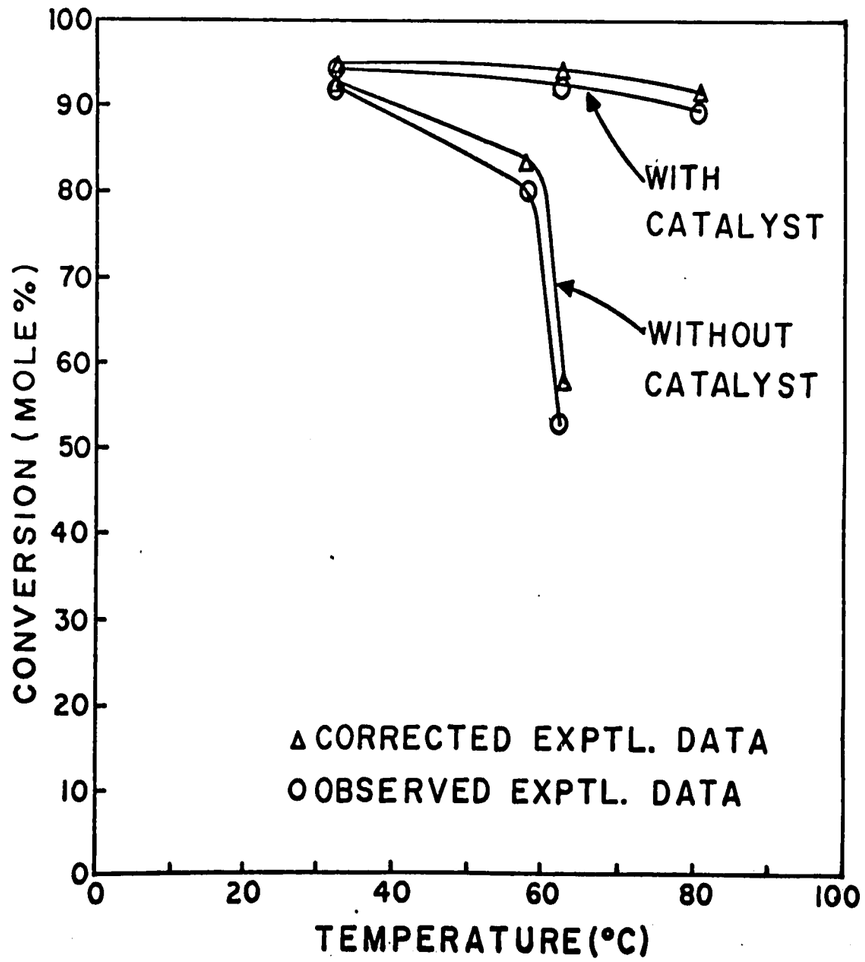


FIG. 25. EFFECT OF TEMPERATURE ON CORRECTED CONVERSION AND YIELD OF ETHYLENE FOR AUTOREFRIGERATED REACTOR WITH CATALYST

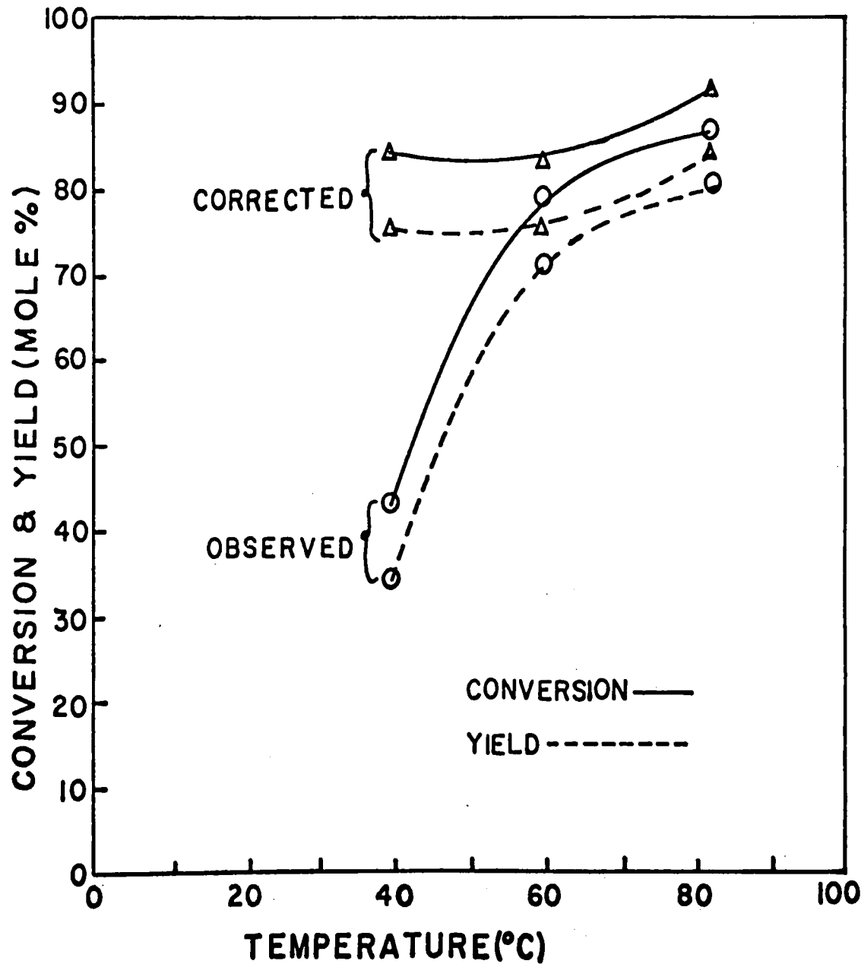


FIG. 26. EFFECT OF MOLAR FEED RATIO ON CORRECTED CONVERSION AND YIELD OF ETHYLENE

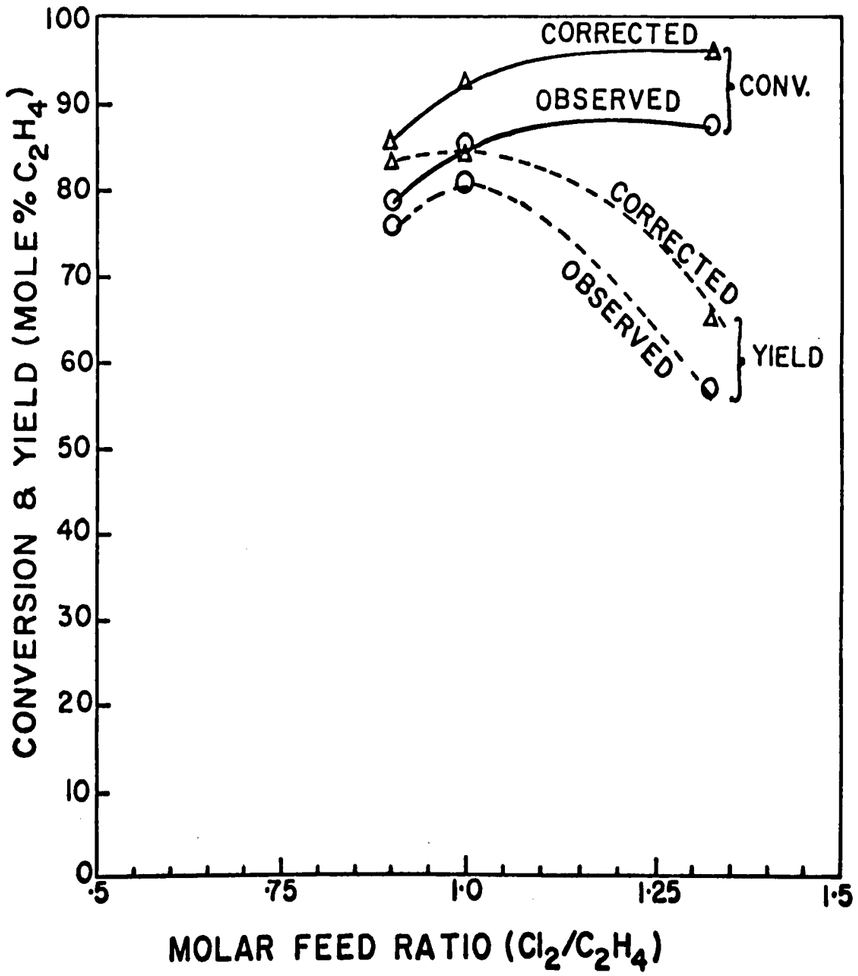
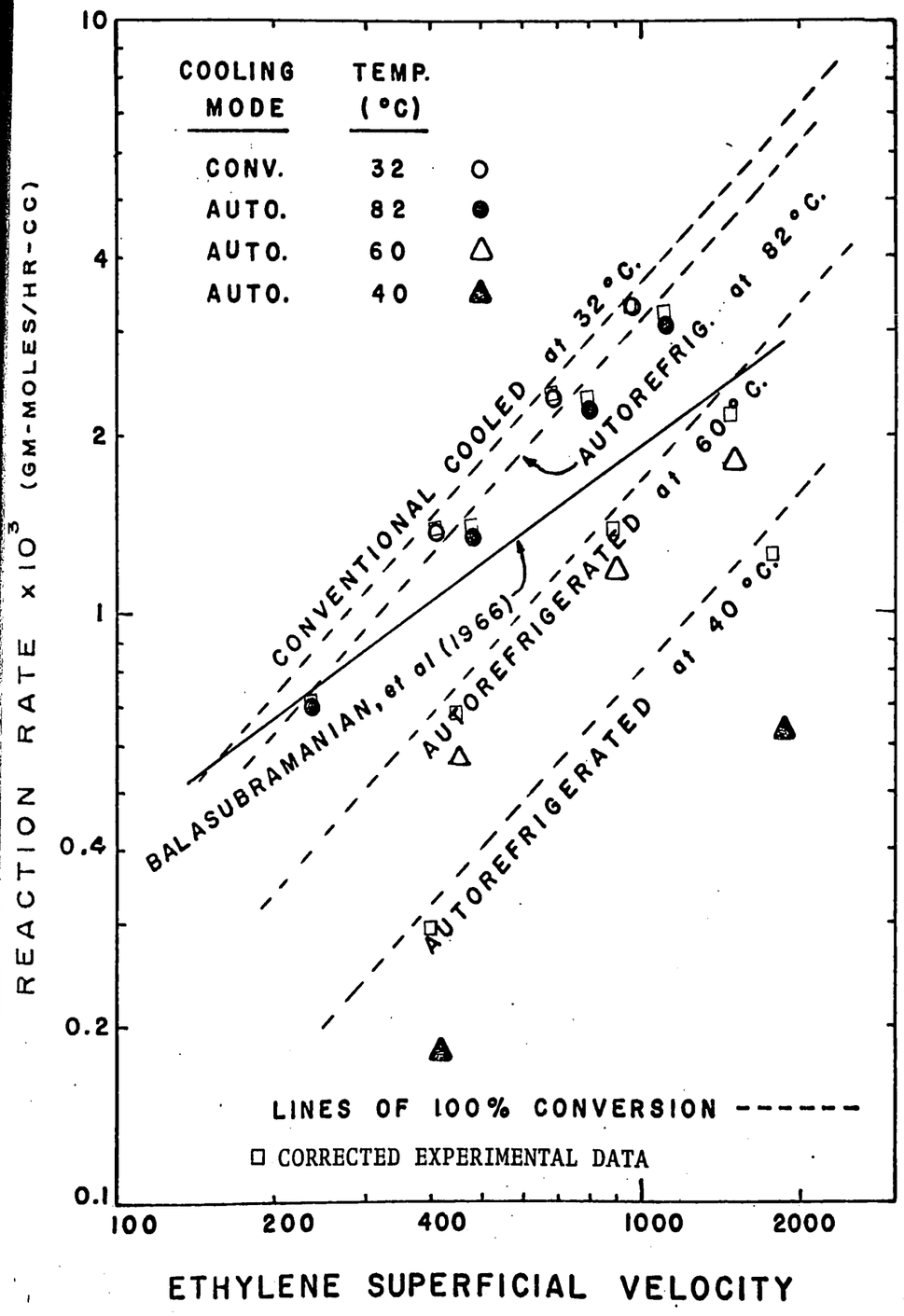


Table 5

Run No.	1	25	6	27	28	29
Cooling Mode	Conv.	Conv.	Conv.	Conv.	Conv.	Auto.
Sparger Type	P	P	P	P	P	P
Catalyst Concn. (g/ℓ)	0.0	0.0	2.0	2.0	2.0	2.0
Operating Mode	Batch	Batch	Batch	Batch	Batch	Batch
Ethylene Feed Rate (cc/min) @ 25°C, 1 atm.	600	1000	600	1000	1400	133
Reactant Feed Ratio (Cl_2/C_2H_4)	1.0	1.0	1.0	1.0	1.0	1.0
Operating Pressure (atm.)	1.0	1.0	1.0	1.0	1.0	2/9
Operating Temperature (°C)	32	32	32	32	32	40
Corrected Conversion (mole % of Ethylene)	92.88	94.88	94.13	95.55	96.44	85.95
Corrected Yield (mole % of Ethylene)	90.88	94.68	93.93	95.55	96.44	81.95
Ethylene Superficial Velocity (cm/hr.)	410	684	410	684	960	420
Reaction Rate$\times 10^3$ (gm-mole/hr.-cc)	1.36	2.34	1.398	2.35	3.32	.292

12	30	13	31	14	33	34	35
Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
P	P	P	P	P	P	P	P
2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Batch	Batch	Batch	Batch	Batch	Cont.	Cont.	Cont.
600	300	600	1000	600	1000	1400	1000
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2/9	1/2	1/2	1/2	1.0	1.0	1.0	1.0
40	60	60	60	82.5	82.5	82.5	82.5
85.00	82.52	82.09	79.97	92.24	92.08	92.4	92.08
76.00	79.52	74.09	68.97	86.24	85.08	85.4	85.08
1889	448	896	1490	477	795	1115	795
1.25	.61	1.22	1.96	1.44	2.32	3.24	1.57

FIG. 27. EFFECT OF ETHYLENE SUPERFICIAL VELOCITY ON CORRECTED REACTION RATE



VIII. MODEL ASSUMING SUBSTITUTION REACTION IN THE BULK LIQUID PHASE

An unfortunate aspect of the reaction system under investigation is added complexity due to side reactions. The substitution reaction is considered the major side reaction. The substitution reaction could occur in (a) the bulk liquid phase, (b) in the bulk vapor phase, (c) in the liquid film, or (d) in any combination of these three phases.

The substitution reaction is assumed to occur in the bulk liquid phase in this chapter. We assume it is an n^{th} order reaction with rate constant k_1, V is the volume of EDC liquid in the reactor.

$$R_S = (C'-Y') \times F_E = k_1(T) \times V \times (C_C^\circ)^n \tag{48}$$

$$k_1(T) \times V = \frac{(C'-Y')\times F_E}{(C_C^\circ)^n} \tag{49}$$

If n=1 , then

$$k_1(T) \times V = \frac{(C'-Y')\times F_E}{C_C^\circ} \tag{50}$$

where R_S = substitution reaction rate.

The modified ethylene volumetric flow rate is the volumetric flow rate of ethylene diluted by EDC such that the partial pressure of EDC would be equal to the vapor pressure of EDC at the reactor temperature.

$$F_E' = F_E \times \frac{P}{(P-P_{ED}')} \times \frac{(T+273)}{298.} \times \frac{1}{P}$$

$$= \frac{F_E \times (T+273)}{298 \times (P-P_{ED}')} \qquad (51)$$

For a film model, assuming no substitution side reaction in the liquid film and the diffusivities of ethylene and chlorine in EDC being equal.

$$R_S + R_{ED} = C' \times F_E = k_L a \times (C_E^* + C_C^\circ) \qquad (52)$$

where R_{ED} is the primary (EDC) reaction rate.

C_C° is the molar concentration of chlorine in the bulk liquid phase (P_C'/H_E) .

Combining Eq. (4) and Eq. (52)

$$k_L a = \frac{C' \times F_E}{\left(\frac{P-P_{ED}}{H_E} + C_C^\circ\right)} \quad \text{where} \quad C_C^\circ = \frac{P_C'}{H_E}$$

$$\therefore k_L a = \frac{C' \times F_E}{\left(\frac{P-P_{ED}}{H_E} + \frac{P_C'}{H_E}\right)} \qquad (53)$$

From Eq. (20)

$$P_E' = (1-C') \times F_E \times P/F \qquad (54)$$

where P_E' is partial pressure of ethylene in the bulk vapor phase.

Table 6 shows the values of $k_l V$, $k_L a$, R_S, P_E', P_C'

Table 6

S. No.	1	2	3	4	5	6
Exptl. Run No.	1	25	6	27	28	29
Cooling Mode	Conv.	Conv.	Conv.	Conv.	Conv.	Auto.
Operating Mode	Batch	Batch	Batch	Batch	Batch	Batch
Sparger Type	P	P	P	P	P	P
Catalyst Concn. (g/ℓ)	0.0	0.0	2.0	2.0	2.0	2.0
Ethylene Feed Rate (cc/min) @ 25°C, 1 atm.	600.	1000.	600.	1000.	1400.	133.
Reactant Feed Ratio (Cl_2/C_2H_4)	1.0	1.0	1.0	1.0	1.0	1.0
Operating Pressure (atm.)	1.0	1.0	1.0	1.0	1.0	2/9
Operating Temperature (°C)	32.0	32.0	32.0	32.0	32.0	40.0
Condenser Reflux Temperature (°C)	12.0	12.0	12.0	12.0	12.0	27.0
Corrected Conversion (mole % of Ethylene)	92.88	94.84	94.13	95.55	96.44	85.95
Corrected Yield (mole % of Ethylene)	90.88	94.64	93.93	95.55	96.44	81.95
Ethylene Partial Pressure in Vapor Phase (atm.)	.4205	.4198	.4198	.4198	.4197	.0052
Chlorine Partial Pressure in Vapor Phase (atm.)	.3092	.4114	.4134	.4278	.4278	.0045
Chlorine Concn. in Liquid Phase$\times 10^5$(gmole/cc)	35.49	47.22	47.45	49.1	49.1	.48
Substitution Reaction Rate$\times 10^5$(gmole/hr.-cc)	2.97	.495	.297	0.0	0.0	1.32
$K_L a \times 10^3$ (1/hr)	3025.1	4093.3	2428.3	3993.6	5641	46634.
Modified Ethylene Volumetric Feed Rate (cc/min)	722.4	1204.	722.4	1204.	1685.5	12421.7

7	8	9	10	11	12	13	14	15
12	2	30	13	31	3	7	8	23
Auto.	Conv.	Auto.	Auto.	Auto.	Conv.	Conv.	Conv.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	P	P	P	P	P	P	P	P
2.0	0.0	2.0	2.0	2.0	0.	2.0	2.0	2.0
600.	600.	300.	600.	1000.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.33
2/9	1.0	1/2	1/2	1/2	1.0	1.0	1.0	1.0
40.0	58.0	60.0	60.0	60.0	62.5	62.5	80.0	81.0
28.5	12.0	15.0	8.0	15.0	13.0	13.0	34.0	34.0
85.0	83.09	82.52	82.09	79.97	58.43	93.81	92.04	95.40
76.0	72.09	79.52	74.09	68.97	20.43	92.81	88.04	64.40
.0054	.2822	.0168	.0182	.0188	.2477	.2379	.0450	.0068
.0027	.1076	.0238	.0169	.0140	.0250	.2233	.0382	.0231
.28	9.28	2.0	1.42	1.18	2.05	18.28	2.57	1.54
13.37	16.34	2.23	11.88	27.23	56.43	1.49	5.94	46.04
305000.	7908.	25008.	64332.	119562.	11577.	5870.	137412.	60933.
55897.	1159.	7735.	15470.	25783.	1349.	1349.	6803.	9391.

16	17	18	19	20	21	22	23	24
14	15	16	17	18	19	33	34	35
Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Cont.	Cont.	Cont.
P	S	T	T	S	S	P	P	P
2.0	1.0	2.0	4.0	4.0	9.3	2.0	2.0	2.0
600.	600.	600.	600.	600.	600.	1000.	1400.	1000.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
48.0	43.0	43.0	50.0	41.5	39.0	43.0	41.0	43.5
92.40	92.08	90.86	92.28	92.40	92.40	92.08	92.4	92.08
86.40	85.08	81.86	86.28	86.40	86.40	85.08	85.4	85.08
.0121	.0134	.0149	.0125	.0121	.0121	.0130	.0133	.0130
.0100	.0062	.0018	.0090	.0100	.0100	.0072	.0062	.0072
.66	.41	.12	.59	.67	.67	.47	.41	.47
8.91	10.37	13.37	8.91	8.91	8.91	17.33	24.26	11.56
149480.	185000.	303270.	149572.	157000.	157000.	285267.	435989.	190200.
22607.	22607.	22607.	22607.	22607.	22607.	37678.6	52750.	37678.6

and F_E' obtained by using corrected conversion and yield data.

Figure 28 and figure 29 are plots of k_La versus F_E' and R_S versus $C_C°$ respectively.

Table 7 represents the detailed heat balance for the reactor and the condenser.

Figure 28 shows that although the value of k_La changes slightly from 40°C to 60°C for the same modified ethylene flow rate, the change is quite pronounced from 60°C to 82.5°C for the same modified ethylene flow rate.

Figure 29 shows that the substitution reaction rate constant at 60°C is higher than substitution reaction rate constant at 82.5°C.

The above mentioned two abnormal behaviors could be due to inherent experimental error in recording the reactor temperature. For autorefrigerated reactor runs, a slight inaccuracy in recording the reactor temperature could cause significant change in the value of chlorine concentration in the bulk liquid phase computed using Eq. (43), Eq. (45), Eq. (46) and Eq. (47). Besides it was found that experimental results of run no. 21, 24 and 32 which are not feasible for autorefrigerated reactor operation at 82.5°C are feasible at slightly lower temperatures.

The reactor temperatures for autorefrigerated runs

Table 7

S. No.	1	2	3	4	5	6
Exptl. Run No.	1	25	6	27	28	29
Cooling Mode	Conv.	Conv.	Conv.	Conv.	Conv.	Auto.
Operating Mode	Batch	Batch	Batch	Batch	Batch	Batch
Sparger Type	P	P	P	P	P	P
Catalyst Concn. (g/ℓ)	0.0	0.0	2.0	2.0	2.0	2.0
Ethylene Feed Rate (cc/min) @ 25°C, 1 atm.	600	1000	600	1000	1400	133
Reactant Feed Ratio (Cl_2/C_2H_4)	1.0	1.0	1.0	1.0	1.0	1.0
Operating Temperature (°C)	32.0	32.0	32.0	32.0	32.0	40.0
Operating Pressure (atm.)	1.0	1.0	1.0	1.0	1.0	2/9
Condenser Reflux Temperature (°C)	12.0	12.0	12.0	12.0	12.0	27.0
Corrected Conversion (mole % of Ethylene)	92.88	94.84	94.13	95.55	96.44	85.95
Corrected Yield (mole % of Ethylene)	90.88	94.64	93.93	95.55	96.44	81.95
Heat Generated in the Reactor (cals/hr)	66116.	111374.	66323.	112085.	158380	13740.
Heat used to Preheat the Reactant Gases (cals/hr)	197.	328.	197.	329.	460.	95.
Heat used to Preheat the Reflux (cals/hr)	14.	19.	13.	17.	19.	720.
Heat used to Vaporize EDC (cals/hr)	310.	375.	256.	324.	363.	12999.
Heat removed by Cooling Water Jacket (cals/hr)	65592.	110649.	65883.	111415.	157538.	0.0
Heat removed in Condenser (cals/hr)	260.	316.	216.	273.	305.	12981.

7	8	9	10	11	12	13	14	15
12	2	30	13	31	3	7	8	23
Auto.	Conv.	Auto.	Auto.	Auto.	Conv.	Conv.	Conv.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	P	P	P	P	P	P	P	P
2.0	0.0	2.0	2.0	2.0	0.0	2.0	2.0	2.0
600.	600.	300.	600.	1000.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.33
40.0	58.0	60.0	60.0	60.0	62.5	62.5	80.0	81.0
2/9	1.0	1/2	1/2	1/2	1.0	1.0	1.0	1.0
28.5	12.0	15.0	8.0	15.0	13.0	13.0	34.0	34.0
85.0	83.09	82.52	82.09	79.97	58.43	93.81	92.04	95.40
76.0	72.09	79.52	74.09	68.97	20.43	92.81	88.04	64.40
63000.	62089.	29355.	60242.	99792.	54865.	65756.	65284.	77639.
427.	961.	510.	1021.	1703.	1098.	1098.	1645.	1908.
3120.	513.	5056.	11693.	17458.	1829.	296.	3435.	13782.
61000.	2550.	23717.	44876.	80879.	8329.	1291.	15264.	59794.
0.0	58085.	0.0	0.0	0.0	43321.	63069.	44939.	0.0
59000.	3076.	28300.	56379.	97600.	10360.	1565.	18500.	72800.

16	17	18	19	20	21	22	23	24
14	15	16	17	18	19	33	34	35
Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Cont.	Cont.	Cont.
P	S	T	T	S	S	P	P	P
2.0	1.0	2.0	4.0	4.0	9.3	2.0	2.0	2.0
600.	600.	600.	600.	600.	600.	1000.	1400.	1000.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
47.0	43.0	43.0	50.0	41.5	39.0	43.0	40.0	43.0
92.40	92.08	90.86	92.28	92.40	92.40	92.08	92.40	92.08
86.40	85.08	81.86	86.28	86.40	86.40	85.08	82.40	85.08
66228.	66247.	66300.	66200.	66380.	66380.	110700.	155400.	110700.
1726.	1726.	1726.	1726.	1726.	1726.	2876.	4027.	2876.
9863.	10541.	10540.	9105.	10800.	10800.	18500.	25210.	18500.
54287.	54500.	55100.	57271.	53900.	54000.	94200.	123863.	94200.
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
64300.	64000.	64000.	63700.	64000.	64000.	107000.	148975.	107000.

FIG. 28. EFFECT OF MODIFIED ETHYLENE FEED RATE ON $K_L a$ FOR BULK LIQUID SUBSTITUTION REACTION MODEL

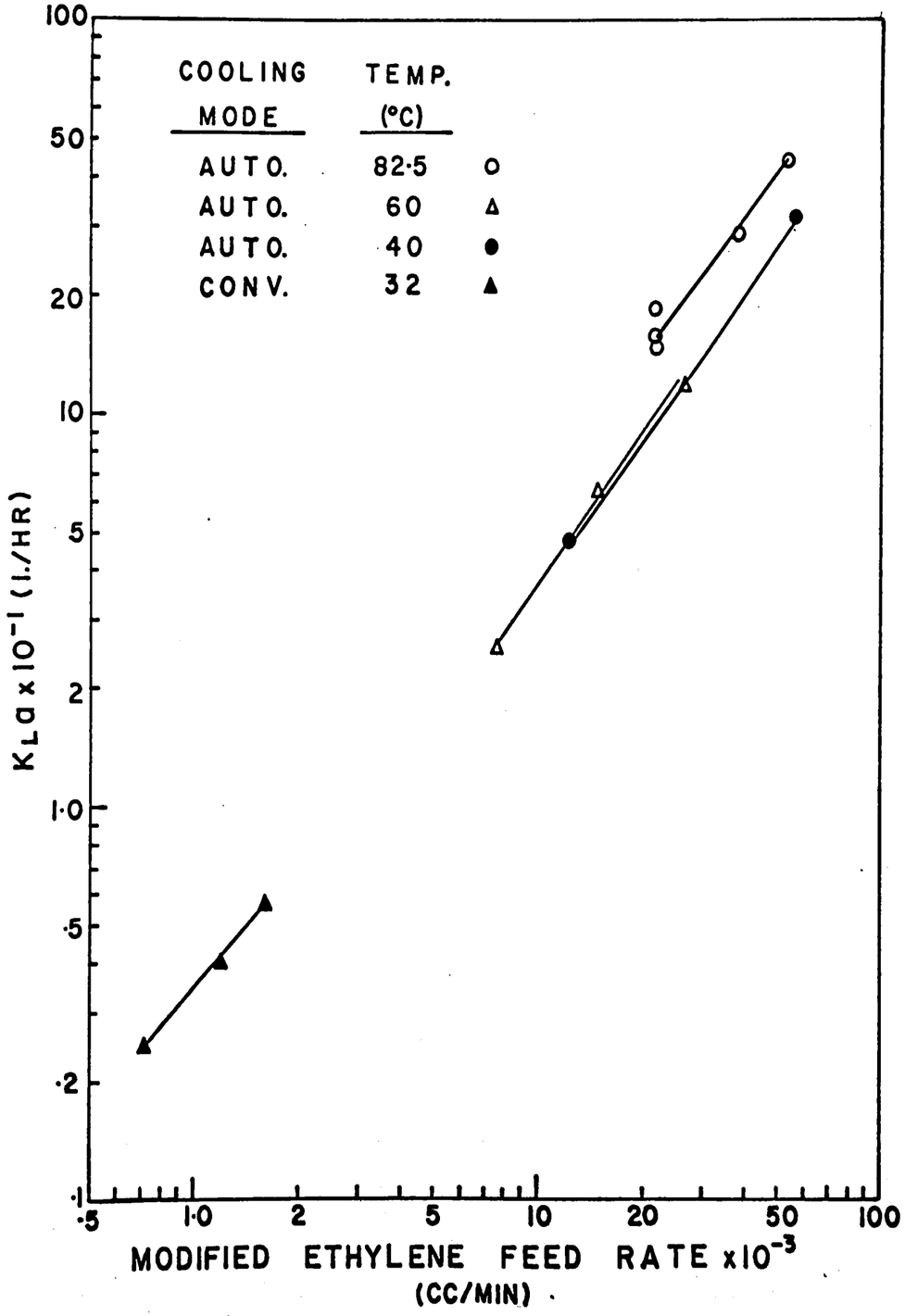
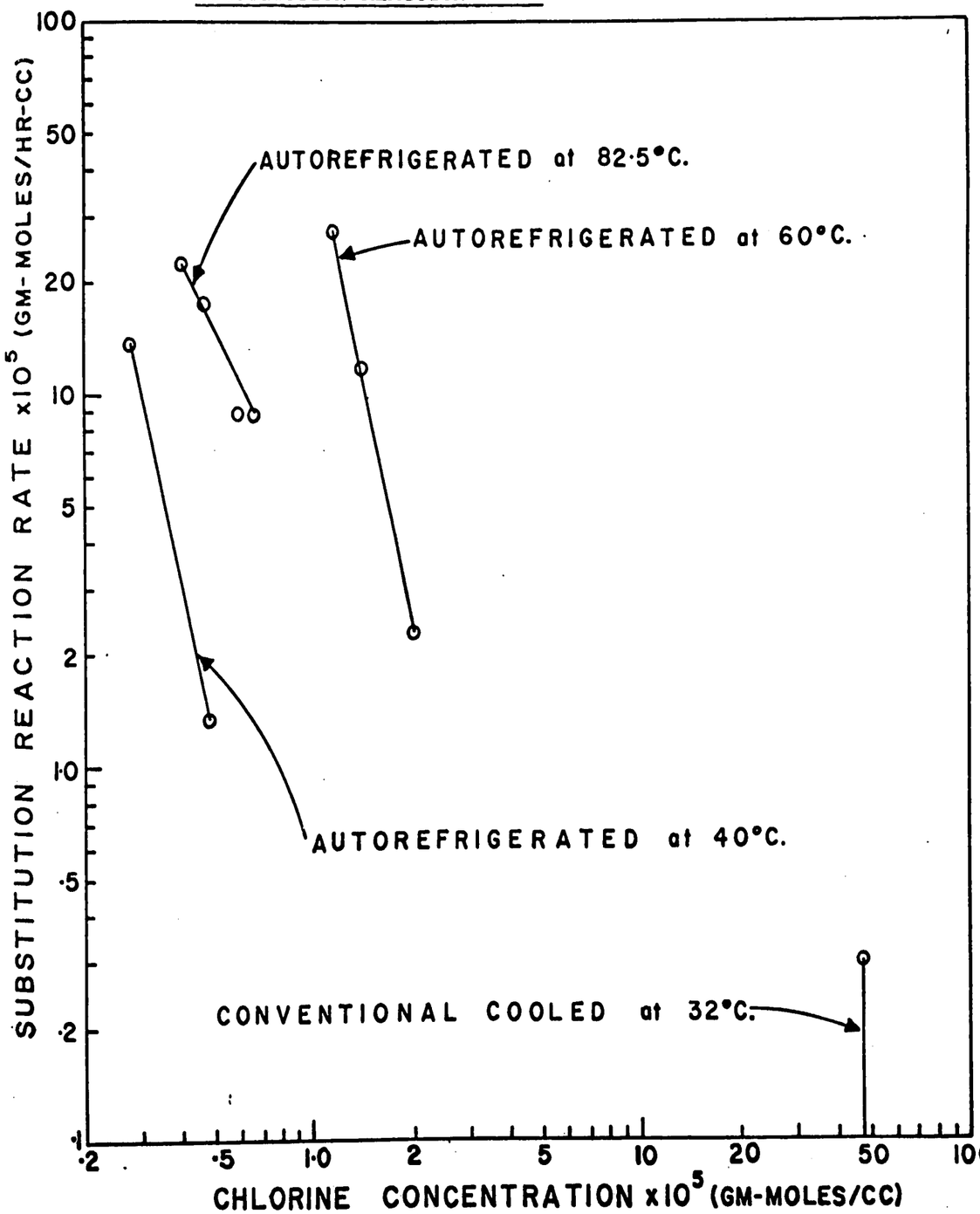


FIG. 29. EFFECT OF BULK LIQUID CHLORINE CONCENTRATION ON SUBSTITUTION REACTION RATE FOR BULK LIQUID SUBSTITUTION REACTION MODEL



at 60°C and 82.5°C, recorded temperatures were adjusted such that:

1. For a given modified ethylene flow rate, $k_L a$ varies very little in the temperature range of interest (40°-82.5°C). In short, $k_L a$ is primarily a function of modified ethylene flow rate in the temperature range of interest.

2. The substitution reaction rate constant obeys Arrehnius' law.

Table 8 shows the values of $k_1 V$, $k_L a$, R_S, P_E', P_C' and F_C' obtained by using conversion and yield data based on corrected autorefrigerated reactor temperatures for autorefrigerated runs at recorded 60°C and 82.5°C temperatures. The correction in reactor temperature never differed by more than 1°C of the recorded reactor temperature.

Figure 30 and figure 31 are plots of $k_L a$ versus F_E' and R_S versus $C_C°$ respectively based on table 8.

The substitution reaction rate could be correlated to reactor temperature and the chlorine concentration in the bulk liquid phase as follows:

$$R_S = e^{56.8} \times e^{-(40.000/RT)} \times (C_C°)^{-4.5} \qquad (55)$$

The nature of Eq. (55) indicates that the substitution reaction rate increases with decrease in bulk liquid phase

Table 8

S. No.	1	2	3	4	5	6
Exptl. Run No.	1	25	6	27	28	29
Cooling Mode	Conv.	Conv.	Conv.	Conv.	Conv.	Auto.
Operative Mode	Batch	Batch	Batch	Batch	Batch	Batch
Sparger Type	P	P	P	P	P	P
Catalyst Concn. (g/ℓ)	0.	0.	2.0	2.0	2.0	2.0
Ethylene Feed Rate (cc/min)	600.	1000.	600.	1000.	1400.	133.
Reactant Feed Ratio Cl_2/C_2H_4	1.0	1.0	1.0	1.0	1.0	1.0
Pressure (atm.)	1.0	1.0	1.0	1.0	1.0	2/9
Reactor Temperature (°C)	32.0	32.0	32.0	32.0	32.0	40.0
Condenser Reflux Temp. (°C)	12.0	12.0	12.0	12.0	12.0	27.0
Corrected Conversion (mole % of C_2H_4)	92.88	94.84	94.13	95.55	96.44	85.95
Corrected Yield (mole % of C_2H_4)	90.88	94.64	93.93	95.55	96.44	81.95
Ethylene Partial Pressure in Vapor Phase (atm.)	.4205	.4198	.4198	.4198	.4197	.0052
Chlorine Partial Pressure in Vapor Phase (atm.)	.3092	.4114	.4134	.4278	.4278	.0045
Chlorine Concn. in Liquid Phase$\times 10^5$(gmole/cc)	35.49	47.22	47.45	49.1	49.1	.48
Substitution Reaction Rate$\times 10^5$(gmole/hr.-cc)	2.97	.495	.297	0.0	0.0	1.32
$K_L a \times 10^3$(1/hr.)	3025.4	4093.24	2428.3	3993.6	5640.5	46633.8
Modified Ethylene Volumetric Feed Rate (cc/min)	722.4	1204.	722.4	1204.	1685.5	12421.7

7	8	9	10	11	12	13	14	15
12	2	30	13	31	3	7	8	23
Auto.	Conv.	Auto.	Auto.	Auto.	Conv.	Conv.	Conv.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	P	P	P	P	P	P	P	P
2.0	0.	2.0	2.0	2.0	0.	2.0	2.0	2.0
600.	600.	300.	600.	1000.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.33
2/9	1.0	1/2	1/2	1/2	1.0	1.0	1.0	1.0
40.0	58.0	60.9	60.9	60.9	62.5	62.5	80.0	81.0
28.5	12.0	31.0	21.0	29.0	13.0	13.0	34.0	34.0
85.0	83.09	87.29	85.99	84.84	58.43	93.81	92.04	95.4
76.0	72.09	84.29	77.99	73.84	20.43	92.81	88.04	64.4
.0054	.2822	.0111	.0120	.0130	.2477	.2379	.0450	.0068
.0027	.1076	.0147	.0097	.0058	.0250	.2233	.0382	.0231
.28	9.28	1.23	.75	.49	2.05	18.28	2.57	1.54
13.36	16.34	2.23	11.88	27.23	56.430	1.48	5.94	46.0
305000.	7908.	43551.	116000.	259982.	11577.	5870.	37412.	60933.
55897.	1158.5	11853.	23706.	39510.	1349.	1349.	6803.	9391.

16	17	18	19	20	21	22	23	24
14	15	16	17	18	19	21	22	24
Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	S	T	T	S	S	P	P	P
2.0	1.0	2.0	4.0	4.0	9.3	2.0	2.0	2.0
600.	600.	600.	600.	600.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
81.6	81.7	81.6	81.6	81.6	82.0	81.5	81.5	81.6
27.0	22.0	23.0	30.0	20.0	25.0	20.0	22.0	37.0
89.02	89.28	87.71	88.92	88.98	91.08	83.0	80.98	83.4
83.02	82.28	78.71	82.92	82.98	85.08	70.0	66.98	81.4
.0203	.0203	.0225	.0199	.0201	.0163	.0230	.0249	.0318
.0270	.0214	.0198	.0277	.0273	.0195	.0198	.0180	.0226
1.79	1.42	1.29	1.83	1.81	1.29	1.32	1.19	1.50
8.91	10.39	13.37	8.91	8.91	8.91	19.3	20.79	2.97
55100.	66690.	70000.	54240.	54600.	76000.	66000.	65794.	59000.
12226.	12878.	12226.	12226.	12226.	15342.	11638.	11638.	12226.

25	26	27	28
32	33	34	35
Auto.	Auto.	Auto.	Auto.
Cont.	Cont.	Cont.	Cont.
P	P	P	P
2.0	2.0	2.0	2.0
300.	1000.	1400.	1000.
1.0	1.0	1.0	1.0
1.0	1.0	1.0	1.0
82.0	81.8	82.0	81.8
47.0	26.0	26.0	26.0
91.32	89.55	90.40	89.55
89.32	82.55	83.40	82.55
.0135	.0185	.0178	.0185
.0300	.0199	.0159	.0199
1.97	1.31	1.04	1.31
1.49	17.33	24.23	11.56
27600.	118000.	205000.	78660.
7671.	22675.	35798.	22675.

FIG. 30. EFFECT OF MODIFIED ETHYLENE FEED RATE ON $K_L a$ FOR BULK LIQUID SUBSTITUTION REACTION MODEL

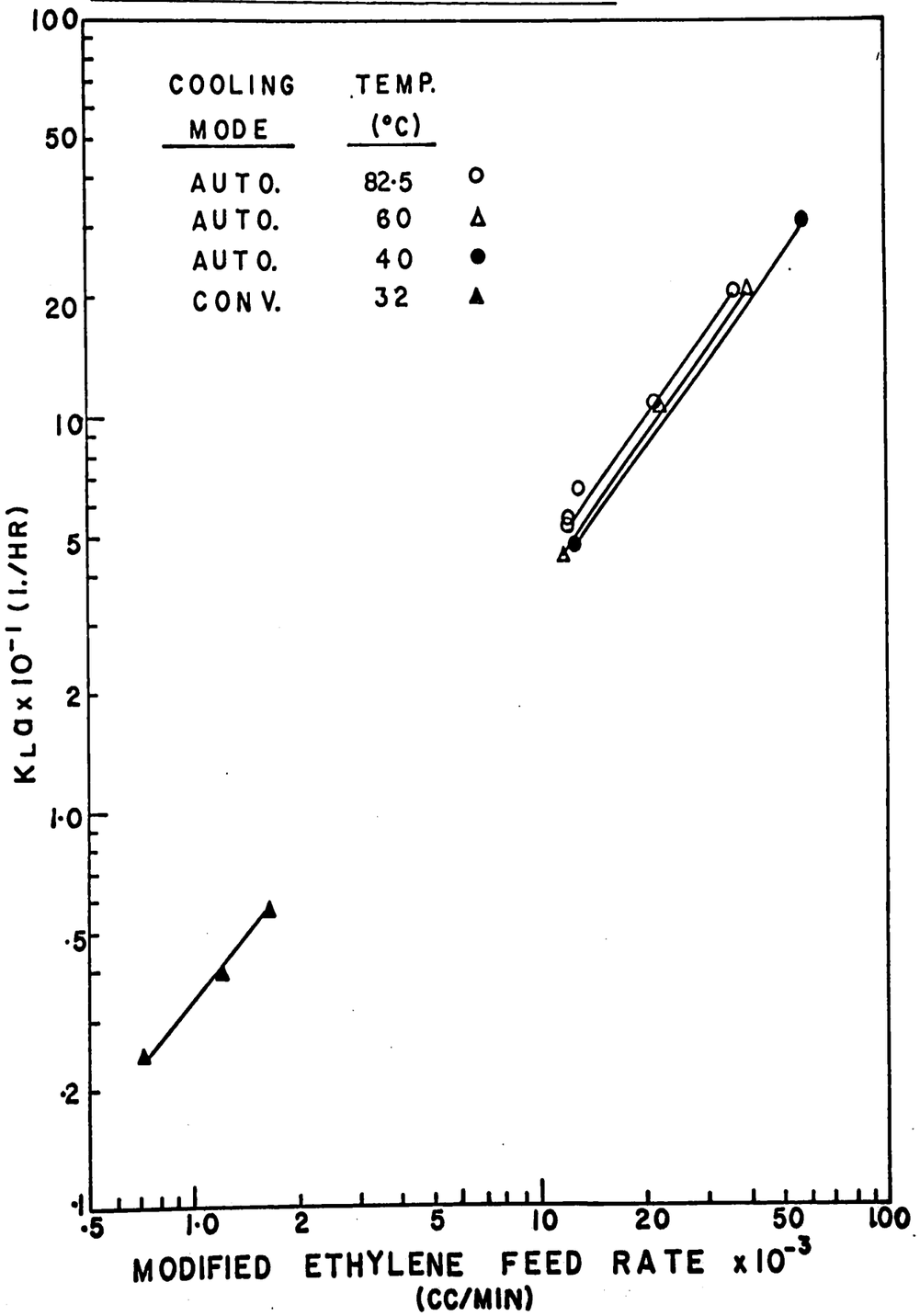
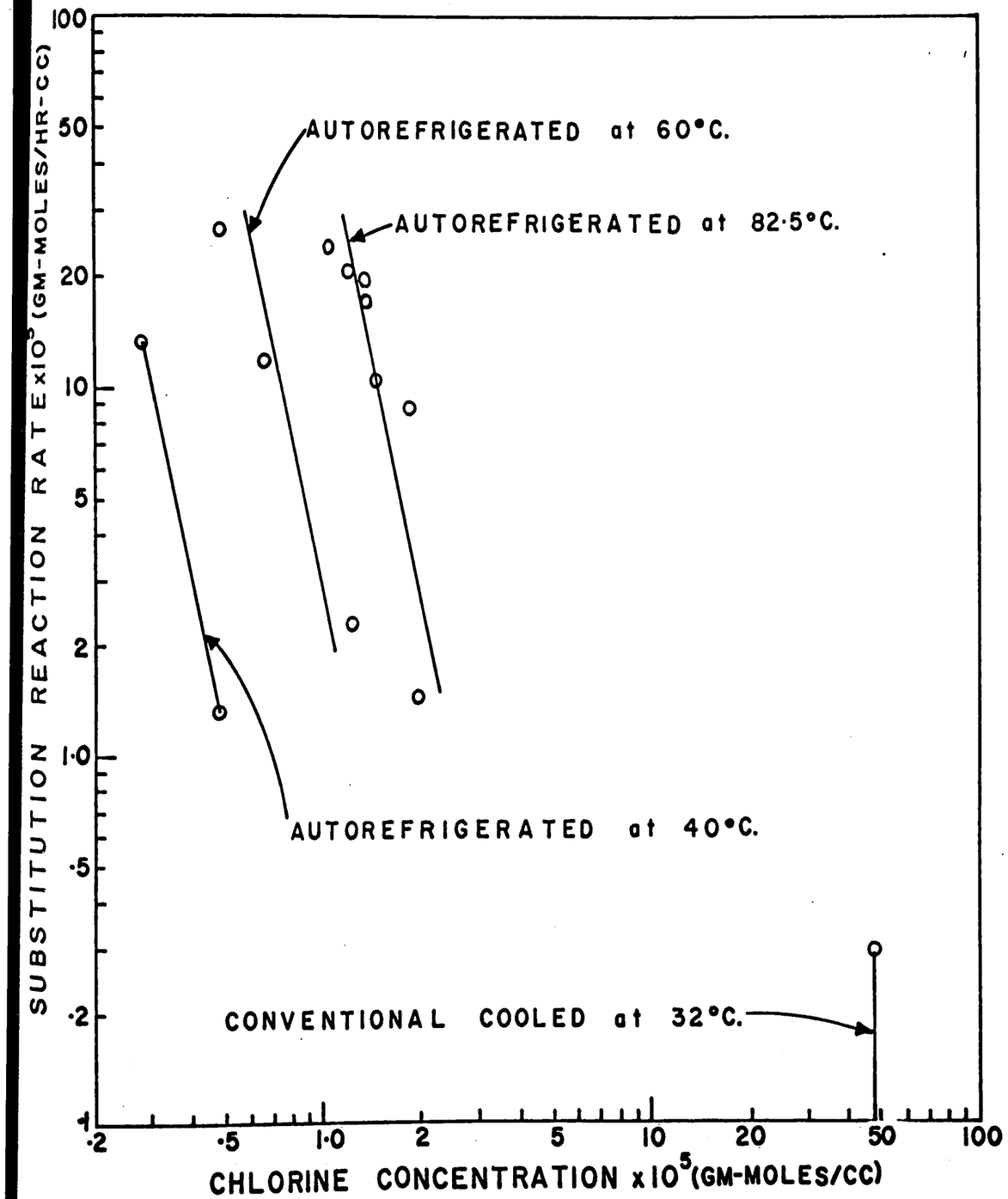


FIG. 31. EFFECT OF BULK LIQUID CHLORINE CONCENTRATION ON SUBSTITUTION REACTION RATE FOR BULK LIQUID SUBSTITUTION REACTION MODEL

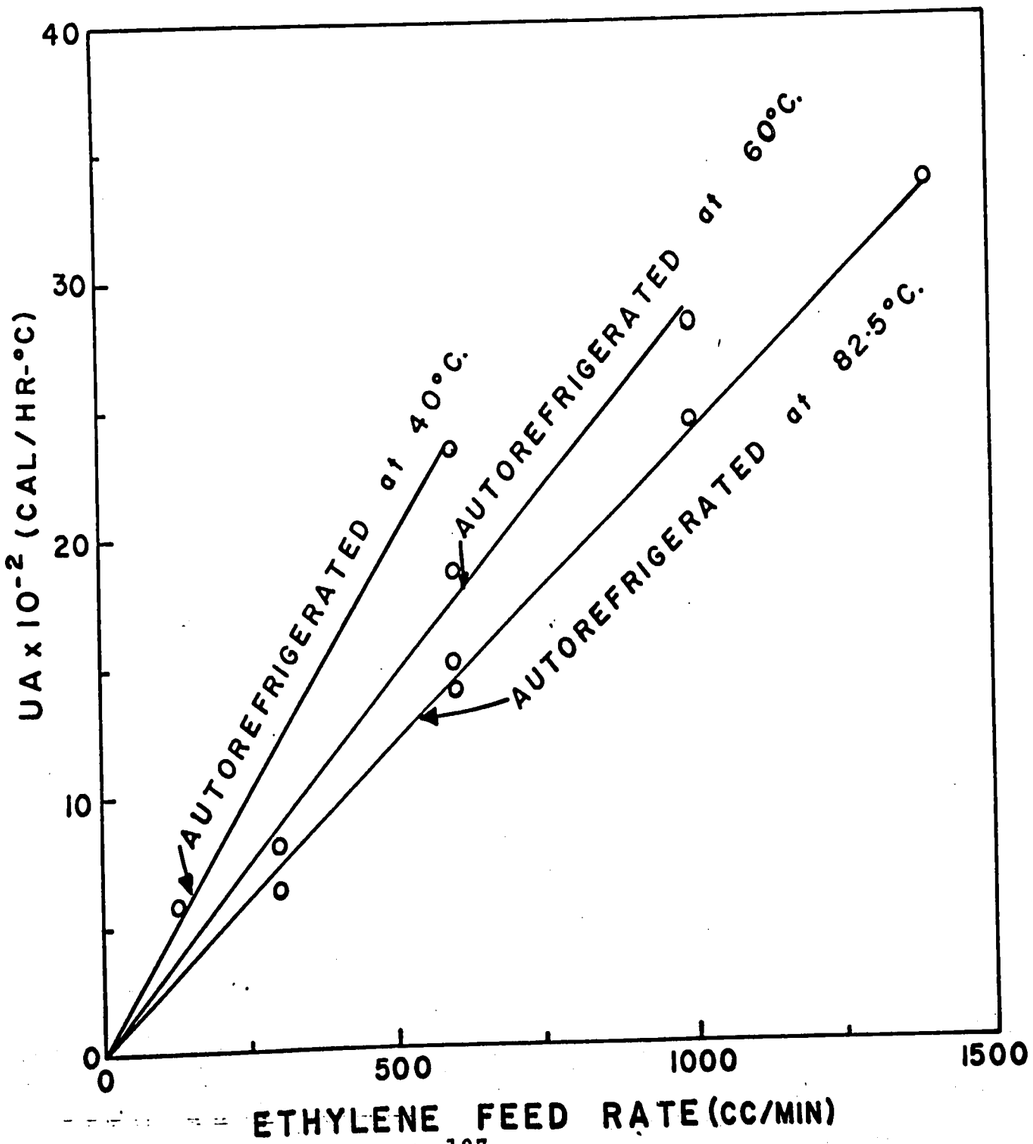


chlorine concentration. This is supported by Seaton's experimental data. During conventionally cooled non-catalytic reactor operation at high reactant gas feed rates (run 26), it was observed that substitution rapidly increased with time after one hour. Since the EDC in the reactor is saturated with chlorine before the reactant feed is begun, it implies low substitution during first one hour period could be due to higher chlorine concentration in the bulk liquid phase.

Figure 32 shows variation of overall heat transfer coefficient (based on arithmatic mean temperature gradient) multiplied by the total heat transfer area of the condenser with ethylene feed rate for autorefrigerated reactor runs at 40°C, 60°C and 82.5°C. The ethylene feed rate is assumed to be approximately proportional to vapor flow rate to condenser from reactor since the conversions of ethylene observed at different reactor temperatures for autorefrigerated reactor runs are approximately equal.

Higher heat transfer coefficients are observed for autorefrigerated reactor operations at lower temperatures for the same ethylene feed rate. This could be due to relatively higher vapor velocities at lower pressures for the same vapor flow rate through the condenser. It results in decrease in gas film (adjacent to condensed liquid film) heat transfer coefficient.

FIG. 32. EFFECT OF ETHYLENE FEED RATE ON OVERALL HEAT TRANSFER COEFFICIENT IN CONDENSER FOR AUTOREFRIGERATED REACTOR OPERATION



The model assuming substitution reaction in the bulk liquid phase gives a reasonable explanation of Seaton's experimental data.

Table 9

S. No.	1	2	3	4	5	6
Exptl. Run No.	1	25	6	27	28	29
Cooling Mode	Conv.	Conv.	Conv.	Conv.	Conv.	Auto.
Operating Mode	Batch	Batch	Batch	Batch	Batch	Batch
Sparger Type	P	P	P	P	P	P
Catalyst Conc. (g/ℓ)	0.0	0.0	2.0	2.0	2.0	2.0
Ethylene Feed Rate (cc/min) @ 25°C, 1 atm.	600.	1000.	600.	1000.	1400.	133.
Reactant Feed Ratio (Cl_2/C_2H_4)	1.0	1.0	1.0	1.0	1.0	1.0
Operating Pressure (atm.)	1.0	1.0	1.0	1.0	1.0	2/9
Operating Temperature (°C)	32.0	32.0	32.0	32.0	32.0	40.0
Condenser Reflux Temperature (°C)	12.0	12.0	12.0	12.0	12.0	27.0
Corrected Conversion (mole % of Ethylene)	92.88	94.88	94.13	95.55	96.44	85.95
Corrected Yield (mole % of Ethylene)	90.88	94.68	93.93	95.55	96.44	81.95
Ethylene Partial Pressure in Vapor Phase (atm.)	.4205	.4198	.4198	.4198	.4197	.0053
Chlorine Partial Pressure in Vapor Phase (atm.)	.3092	.4134	.4134	.4281	.4278	.0045
Exptl. Substitution Reaction Rate$\times 10^5$ (gmoles/hr.-cc)	2.97	.495	.297	0.0	0.0	1.32
Theoretical Substitution Reaction Rate$\times 10^5$ (gmoles/hr.-cc)	1.33	1.17	1.17	1.15	1.15	1.29

7	8	9	10	11	12	13	14	15
12	2	30	13	31	3	7	8	23
Auto.	Conv.	Auto.	Auto.	Auto.	Conv.	Conv.	Conv.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	P	P	P	P	P	P	P	P
2.0	0.0	2.0	2.0	2.0	0.0	2.0	2.0	2.0
600.	600.	300.	600.	1000.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.33
2/9	1.0	1/2	1/2	1/2	1.0	1.0	1.0	1.0
40.0	58.0	60.0	60.0	60.0	62.5	62.5	80.0	81.0
28.0	13.0	13.0	12.0	13.0	13.0	13.0	35.0	37.0
84.11	83.19	82.05	82.95	79.63	58.43	93.81	92.04	95.91
75.11	72.19	79.05	74.95	68.63	20.43	92.81	88.04	64.91
.0054	.2822	.0167	.0182	.0192	.2477	.2377	.045	.0062
.0028	.1065	.0236	.0162	.0138	.0250	.2231	.038	.0196
13.37	16.34	2.23	11.88	27.23	56.43	1.485	.0594	46.04
1.53	4.33	4.73	5.79	6.05	8.88	3.49	.0821	7.33

16	17	18	19	20	21	22	23	24
14	15	16	17	18	19	20	21	22
Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.	Auto.
Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch	Batch
P	S	T	T	S	S	P	P	P
2.0	1.0	2.0	4.0	4.0	9.3	2.0	2.0	2.0
600.	600.	600.	600.	600.	600.	600.	600.	600.
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5
47.0	44.0	40.0	48.0	40.0	40.0	25.0	37.0	37.0
92.21	92.08	90.3	91.86	92.24	92.9	76.67	86.3	84.3
86.21	85.08	81.3	85.86	86.24	86.9	55.67	73.3	70.3
.0123	.0130	.0135	.0121	.0116	.0125	.0135	.0141	.0141
.0094	.0072	.0058	.0100	.0109	.0084	.0065	.0045	.0045
8.91	10.39	13.37	8.91	8.91	8.91	31.19	19.30	20.79
12.03	13.64	18.88	11.33	10.96	14.59	45.82	45.85	45.82

25	26	27	28	29
24	32	33	34	35
Auto.	Auto.	Auto.	Auto.	Auto.
Batch	Cont.	Cont.	Cont.	Cont.
P	P	P	P	P
2.0	2.0	2.0	2.0	2.0
600.	300.	1000.	1400.	1000.
0.9	1.0	1.0	1.0	1.0
1.0	1.0	1.0	1.0	1.0
82.5	82.5	82.5	82.5	82.5
47.0	49.0	43.0	41.0	43.0
85.55	92.07	92.08	92.4	92.08
83.55	90.07	85.08	85.4	85.08
.0174	.0051	.0130	.0133	.0130
.0118	.0254	.0072	.0062	.0072
2.97	1.49	17.33	24.26	11.6
11.78	7.24	13.64	14.56	13.64

IX. MODEL ASSUMING SUBSTITUTION REACTION IN THE ETHYLENE LIQUID FILM

Danckwerts (2) summarizes the theoretical and experimental study of gas absorption with chemical reaction occurring in the liquid film. Analytic solution has been obtained for irreversible m^{th} order reactions when the reaction rate of the dissolved gas is proportional to m^{th} power of its concentration, instantaneous irreversible reaction when the dissolved gas reacts with dissolved reactant (in the bulk phase), and irreversible second-order reaction when the dissolved gas reacts with a dissolved reactant (in the bulk phase) by a second order reaction.

No analytic solution is possible when more than one, simultaneous second-order and higher order reactions occur in the liquid film (between the dissolved gas the dissolved reactant in the bulk phase).

In chlorination of ethylene it is possible that the substitution reaction takes place in the ethylene liquid film when one molecule of ethylene reacts with two molecules of chlorine to give trichloroethane. Simultaneously, the main reaction involving reaction between an ethylene molecule and a chlorine molecule forms ethylene dichloride. The liquid film model is depicted in figure 33. The reactions are assumed not to be instantaneous.

The molar concentration of chlorine in the bulk liquid phase is C_C° . The chlorine diffuses from the bulk liquid phase in the ethylene liquid film and reacts with ethylene diffusing in an opposite direction. The two simultaneous reactions producing ethylene dichloride and trichloroethane occur in the liquid film. The reaction producing dichloroethane is assumed to be a second-order irreversible reaction while the other reaction is assumed to be a third order irreversible reaction.

$$R_E = k_1 \times C_E \times C_C$$

R_E - rate of EDC production.

$$R_S = k_2 \times C_E \times (C_C)^2$$

where R_S - substitution reaction rate.

The rate of diffusion into and out of the element is equal to the sum of rate of accumulation and rate of reaction for a particular component. As steady state rate of accumulation is zero.

Chlorine:

$$D_C \frac{\partial^2 C_C}{\partial X^2} = k_1 C_E \cdot C_C + 2k_2 (C_E)(C_C^2) \qquad (55)$$

Where C_E , and C_C are concentration of ethylene and chlorine and x is the distance from the gas liquid interface.

Ethylene:

$$D_E \frac{\partial^2 C_E}{\partial X^2} = k_1 C_E \cdot C_C + k_2 (C_E)(C_C)^2 \qquad (56)$$

let

$$A = C_E / C_E^* \ , \qquad (57)$$

$$B = C_B / C_B^\circ \qquad (58)$$

and

$$X = x/\delta \qquad (59)$$

where δ is the film thickness.

Combine Eq. (55), Eq. (56), Eq. (57), Eq. (58) and Eq. (59)

$$\frac{d^2A}{dX^2} = \left(\frac{\delta^2 k_1 C_C^\circ}{D_E}\right)AB + \left(\frac{k_2 \delta^2 \cdot C_C^{\circ 2}}{D_E}\right)AB^2 \qquad (60)$$

$$\frac{d^2B}{dX^2} = \left(\frac{\delta^2 k_1 C_E^*}{D_C}\right)AB + \left(\frac{2k_2 \delta^2 C_E^{*2}}{D_C}\right)AB^2 \qquad (61)$$

Eq. (60) and Eq. (61) can be simplified to

$$\frac{d^2A}{dX^2} = C_1\left(\frac{C_C^\circ}{D_E}\right)\cdot A \cdot B + C_2 \cdot \left(\frac{C_C^{\circ 2}}{D_E}\right)AB^2 \qquad (62)$$

$$\frac{d^2B}{dX^2} = C_1\left(\frac{C_E^*}{D_C}\right)AB + C_2\left(\frac{2C_E^{*2}}{D_C}\right)AB^2 \qquad (63)$$

where $C_1 = \delta^2 k_1$, $C_2 = \delta^2 k_2$.

The boundary conditions are

$X = 0 \qquad A = 1$

$X = 1 \qquad B = 1 \ ; \qquad A = 0$

We have three boundary conditions and to solve

Eq. (62) and Eq. (63) for a given value of C_1 and C_2 requires four boundary conditions. Attempt was made to solve these differential equations numerically assuming B=0 at (X=0) the gas liquid interface. Value of C_1 was assumed and C_2 varied such that A=0 at X=1. Then the value of B at X=1.0 was checked and depending on whether it was less than or greater than one, a new value of C_1 assumed and the procedure repeated. However, it was found that it is physically impossible to get a set of values of (C_1,C_2) such that the boundary conditions mentioned below could be satisfied.

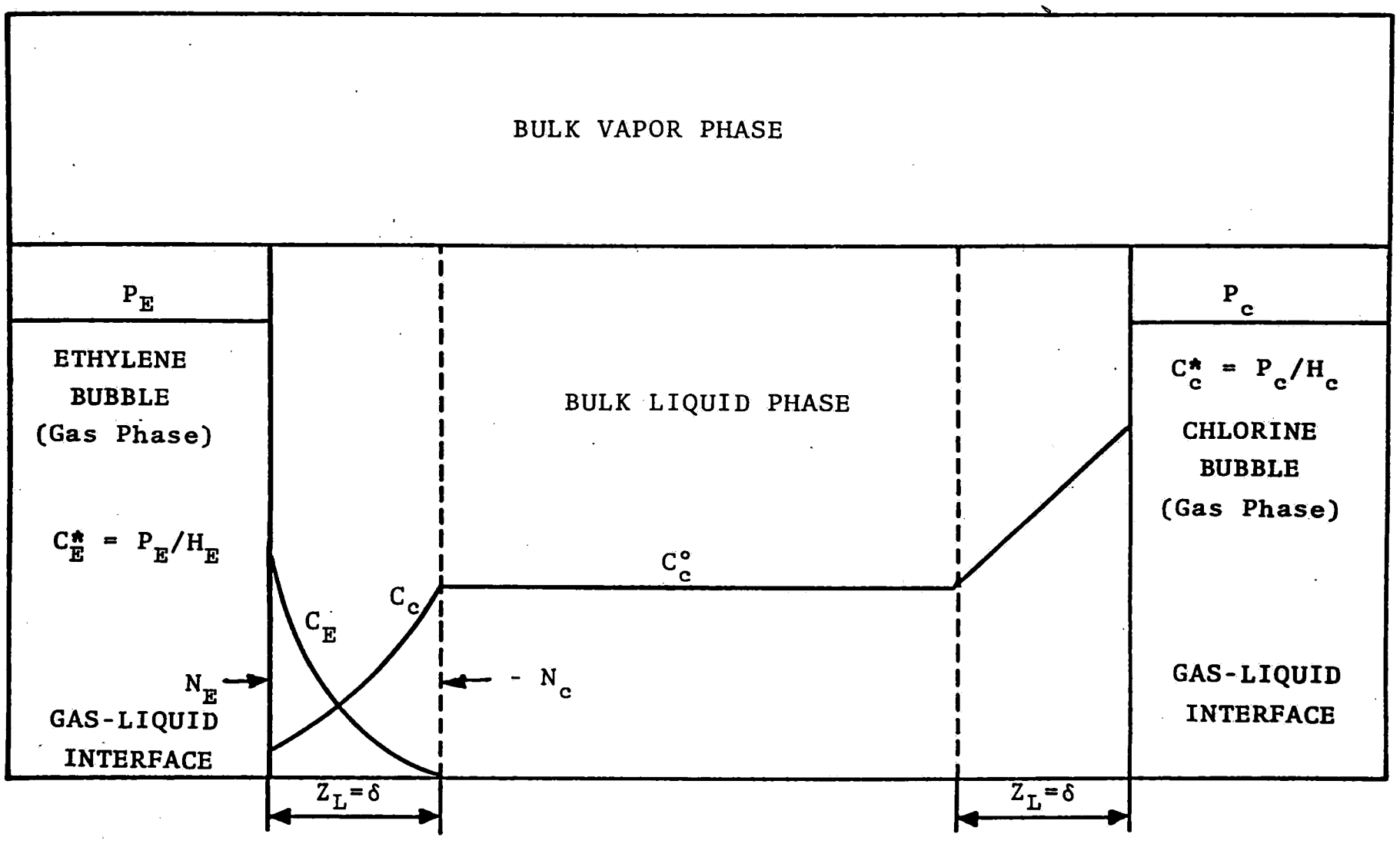
X = 0 A = 1 B = 0

X = 1 B = 1 A = 0

However, it is obvious that this model can not explain Seaton's experimental data.

1) It is observed that the substitution increases as the bulk liquid concentration of chlorine decreases for autorefrigerated runs at 40°C and 60°C. At higher chlorine concentration the substitution reaction is selectively favored over the main reaction. Hence, this model predicts higher substitution when the chlorine concentration in the bulk phase is higher.

FIG. 33. FILM THEORY MODEL FOR ETHYLENE-CHLORINE REACTIONS IN THE LIQUID FILM



X. SUBSTITUTION REACTION IN THE BULK VAPOR PHASE

As discussed earlier in chapter V, there is a possibility of the main reaction producing dichloroethane and/or the substitution reaction producing trichloroethane occurring in the bulk vapor phase. However, the kinetic data on vapor phase chlorination of ethylene is scarce and very specific in nature. (Valid only under certain specified reaction conditions.) A reaction model was tested for consistency in light of Seaton's experimental data for the following assumption.

1) The main reaction producing dichloroethane occurs in the liquid phase.

2) The substitution reaction occurs in the bulk vapor phase. The reaction is m^{th}, n^{th} order in ethylene and chlorine concentrations in the bulk vapor phase respectively.

$$R_S = k_V \cdot V \cdot (P_E')^m (P_C')^n \qquad (64)$$

where R_S is the substitution reaction rate.

V is the volume of the vapor phase.

3) The reaction constant varies with temperature according to Arrehnius' law.

$$k_V = Ae^{-B/T} \qquad (65)$$

All the assumptions made in chapter VII hold good.

Combining Eq. (64) and Eq. (65)

$$R_S = Ae^{-B/T} V (P_E')^m (P_C')^n \qquad (66)$$

From Eq. (66)

$$\ell n\, R_S = \ell n(AV) - B/T + m\, \ell n\, P_E' + n\, \ell n\, P_C' \qquad (67)$$

Eq. (67) could be represented as

$$Y_i = A' + Bx_{1i} + mx_{2i} + nx_{3i} \qquad (68)$$

where $Y_i = \ell n\, R_S$, $x_{1i} = -1/T$, $x_{2i} = \ell n\, P_E'$, $x_{3i} = \ell n\, P_C'$ and $A = \ell n(AV)$

$$\text{let } Y_i = \ell n\, R_S^E$$

where R_S^E is the observed values of substitution reaction rate.

The values of A', B, m and n were obtained by method of least squares such that $\Sigma(Y_i - Y_i)^2$ is minimum for Seaton's experimental data.

$A' = 5.7331$, $B = 3163.1935$, $m = .21$, $n = -.43$

Table 10 summarizes the observed substitution reaction rate and the substitution reaction rate predicted by Eq. (66).

This model is inconsistent with Seaton's experimental data, because

1) The reaction rate is proportional to negative power of chlorine concentration in the bulk vapor phase. This is hardly possible kinetically. It means the reaction rate increases as chlorine concentration decreases.

2) Although the observed substitution reaction rate and calculated substitution reaction rate are in reasonable agreement for most of the experimental data at 82.5°C, it shows deviation of 200% and larger at other temperatures.

3) At 32°C, the substitution reaction rate is zero (run 27, run 28) when higher concentrations of ethylene and chlorine in the bulk vapor phase are encountered.

4) In run 35, compared to run 33, the volume of the bulk vapor phase is smaller and the ethylene and chlorine concentrations in the bulk vapor phase are equal, yet the same substitution reaction rate is observed.

XI. CONCLUSIONS

1) The model assuming that substitution reaction occurs in the bulk liquid phase gives a reasonable explanation of Seaton's experimental data.

2) For the same exit gas temperature, the EDC loss via condenser were found to be significant at low pressure autorefrigerated operations. In such cases, low temperature cooling liquid should be circulated through the condenser to arrest the EDC loss.

3) Although it was observed that the best performance of the autorefrigerated reactor was lower than that of conventionally cooled reactor, it is possible that the autorefrigerated reactor performance at pressures greater than 1 atm. could improve.

APPENDIX A

PROPERTIES OF 1,2-DICHLOROETHANE (EDC)

(27,35,36,37)

1) Chemical Formula: $C_2H_4Cl_2$

2) Formula Weight: 98.97

3) Melting Point: -35.3°C

4) Boiling Point: 83.5°C @ 1 atm.

5) Critical Constants: T_c = 288.4°C = 561°K

P_c = 53.0 atm.

d_c = 0.45 g/cc

v_c = 220 - 225 cc/mole

Z_c = 0.299

6) Latent Heat of Vaporization: ΔH_v = 8440 cal/mole @ 0°C

= 8300 cal/mole @ 25°C

= 8240 cal/mole @ 32°C

= 8170 cal/mole @ 40°C

= 7650 cal/mole @ 83.5°C

7) Vapor Pressure: (See Figure A-1)

8) Heat of Combustion: ΔH_c° = -296,770 cal/mole @ 298°K (liquid)

9) Heat of Formation: ΔH_f° = -39,700 cal/mole @ 298°K (liquid)

10) Density (liquid): $d_T = d_s + (c_1)(T-T_s) + (c_2)(T-T_s)^2 + (c_3)(T-T_s)^3$

where: T_s = 0°C

d_s = 1.28248

$c_1 = -1.4217 \times 10^{-3}$

$c_2 = -0.933 \times 10^{-6}$

$c_3 = 2.29 \times 10^{-9}$

d = 1.28248 g/cc @ 0°C

= 1.24640 g/cc @ 25°C

= 1.23612 g/cc @ 32°C

= 1.22517 g/cc @ 40°C

= 1.16736 g/cc @ 83°C

11) Viscosity (liquid): μ = 1.10 centipoise @ 0°C
0.80 centipoise @ 25°C
0.74 centipoise @ 32°C
0.68 centipoise @ 40°C
0.43 centipoise @ 83°C

12) Specific Heat (liquid): $c_P = 28.7987 + (8.3475\times10^{-3})T$, cal/(mole)(°C)
= 27.63 @ -30°C
= 29.76 @ +20°C
= 30.18 @ 30°C
= 31.13 @ 50°C
= 31.58 @ 60°C
= 32.5 @ 83°C

13) Mean Gas c_P = 0.96 cal/(mole)(°C), 111°-221°C

14) Thermal Conductivity (liquid): k = 0.082 BTU/(hr)(ft^2)(°F/ft)@122°F

15) Pitzer Accentric Factor = 0.301 (T_s=393°K, P_s=2.65 atm.)

16) Estimation of molar volume at normal boiling point:

2 ea. (-C-)'s @ 14.8 = 29.6
2 ea. (-Cl)'s @ 21.6 = 43.2
4 ea. (-H)'s @ 3.7 = 14.8
V_o = 87.6 cc/mole

17) Estimation of the Force Constant, ε/k

$\varepsilon/k = 0.77T_c$ = 432°K
$= 1.15T_b$ = 410°K
$= 1.92T_m$ = 456°K

18) Estimation of the Collision Diameter, r_o

$$r_o = 1.18V_o^{1/3} = 1.18 \times 4.441 = 5.240 \text{ Å}$$

19) Solubility in water = 0.9 g/100 g H_2O

Primary source of the above data is Perry, J. H., (ed.), "Chemical Engineers' Handbook," 4th Ed., McGraw-Hill, New York (1963). Other references include:

"International Critical Tables," McGraw-Hill, New York (1929).

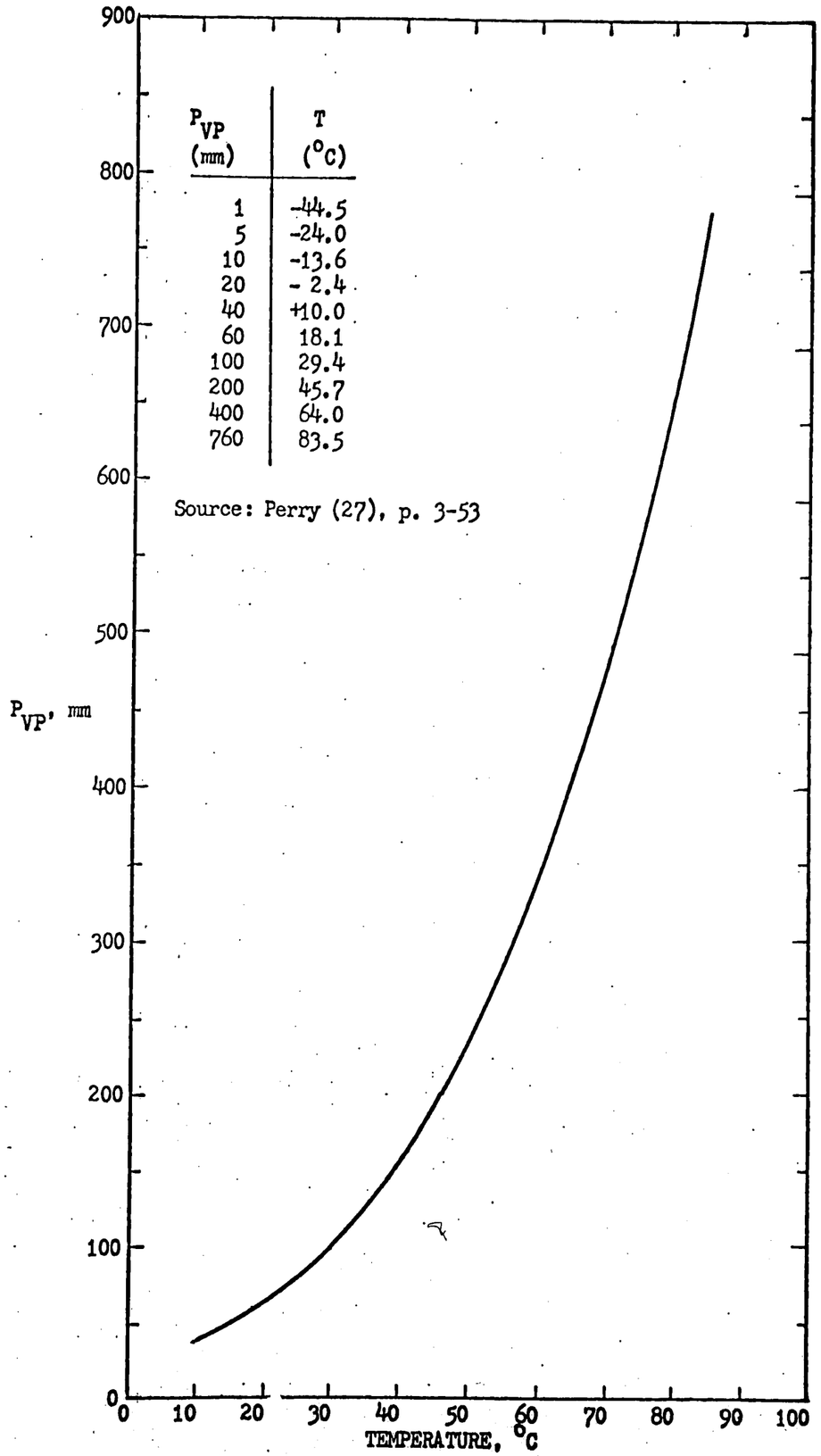
Stull et al., "The Thermodynamics of Organic Compounds," John Wiley, New York (1969).

Hildebrand, J. H. and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N.J. (1962).

FIG. A-1 VAPOR PRESSURE CURVE FOR 1,2-DICHLOROETHANE (EDC)

P_{VP} (mm)	T (°C)
1	-44.5
5	-24.0
10	-13.6
20	- 2.4
40	+10.0
60	18.1
100	29.4
200	45.7
400	64.0
760	83.5

Source: Perry (27), p. 3-53



APPENDIX B

PROPERTIES OF CHLORINE

1) Chemical Formula: Cl_2

2) Formula Weight: 70.91

3) Melting Point: -101.6°C

4) Boiling Point: - 33.8°C

5) Critical Constants:
T_c = 144°C = 416°K
P_c = 76.1 atm.
d_c = 0.573 g/cc
$\bar{v}_c$ = 123.8 cc/mole
Z_c = 0.276

6) Density at 0°C, 1 atm. = 3.2204 g/l (0.2011 lb/ft^3)

7) Molar volume at 1 atm.: (calculated)
$\bar{v}$ = 22,010 cc/mole @ 0°C
= 24,025 cc/mole @ 25°C
= 24,600 cc/mole @ 32°C
= 25,270 cc/mole @ 40°C
= 28,720 cc/mole @ 83°C

8) Latent Heats: Fusion: 1531 cal/mole (-101.6°C)
Vaporization: 4878 cal/mole (-33.8°C)

9) Heat Capacity: (Ideal gas state)

$$c_P^* = 7.576 + (2.424\times10^{-3})T + (-0.965\times10^{-6})T^2$$

10) c_p/c_v = 1.355 @ 15°C

11) Viscosity: μ = 0.0128 centipoise @ 0°C
= 0.0139 centipoise @ 25°C
= 0.0142 centipoise @ 32°C
= 0.0145 centipoise @ 40°C
= 0.0160 centipoise @ 83°C
μ_c = 0.0420

12) Thermal Conductivity:

$k = 0.0043$ BTU/(hr)(ft^2)(°F/ft) @ 32°C

13) Molar volume at normal boiling point = 48.4 cc/mole = V_o

14) Collision diameter, $r_o = 4.115$ Å

15) Force constant, $\varepsilon/k = 357°K$

16) Calculated diffusivity in EDC from Wilke-Chang equation:

$D_B = 3.22\times10^{-5}$ cm^2/sec (32°C)

(Balasubramanian et al.: 2.92×10^{-5} cm^2/sec)

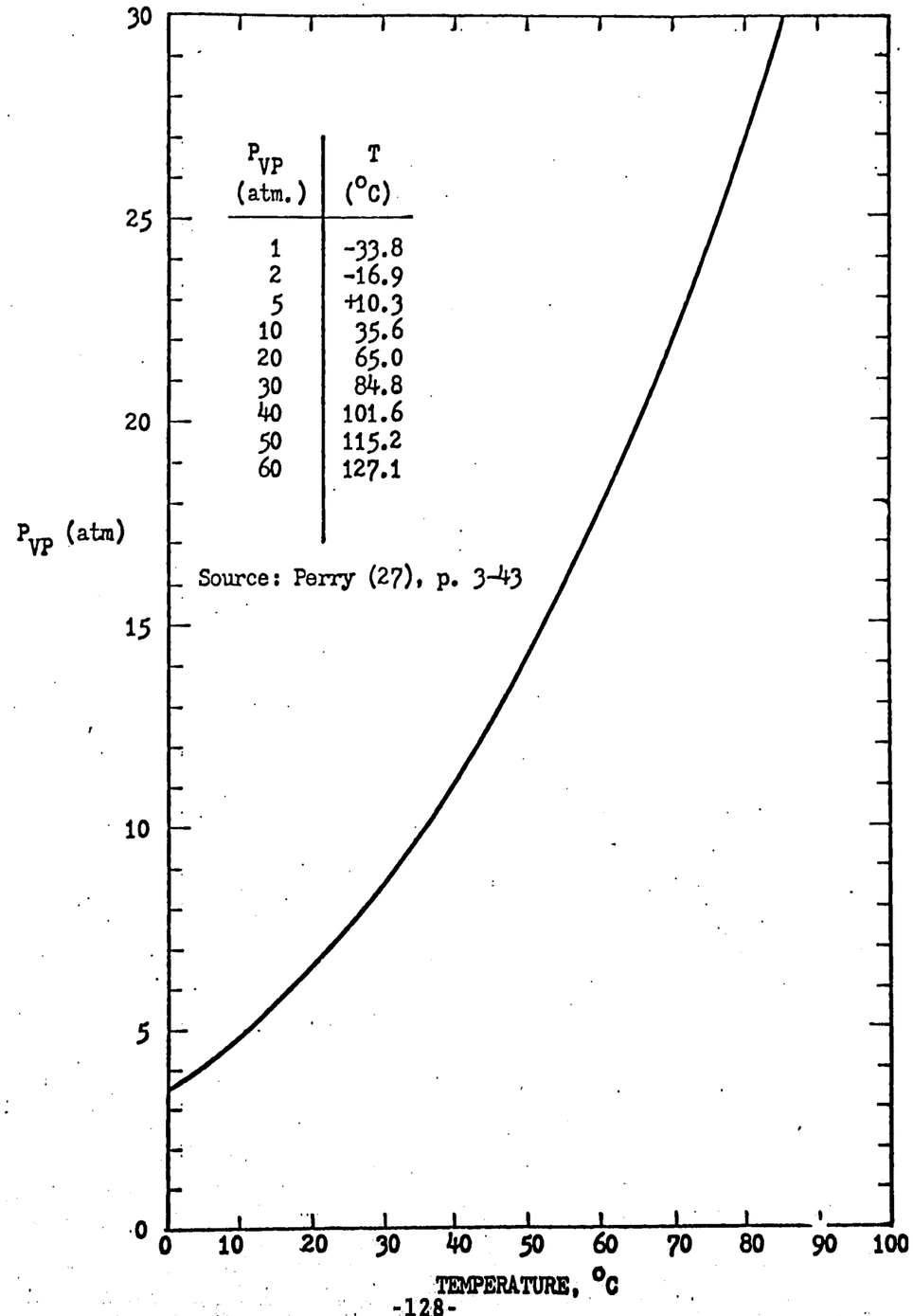
17) Henry's Law constant for Cl_2 in EDC: (Balasubramanian et al.)

$H_B = 0.477\times10^{4}$ atm (cc/mole) @ 32°C, 1 atm.

18) Pitzer Accentric Factor = 0.076 (T_s=19°C, P_s=6.4 atm.)

Primary source of the above data is Perry, J. H. (ed.), "Chemical Engineers' Handbook," 4th edition, McGraw-Hill, New York (1963).

FIG. B-1 VAPOR PRESSURE CURVE FOR CHLORINE



APPENDIX C

PROPERTIES OF ETHYLENE

1) Chemical Formula: $CH_2:Ch_2$

2) Formula Weight: 28.05

3) Melting Point: -169.0°C

4) Boiling Point: -103.7°C @ 1 atm.

5) Density @ 0°C, 1 atm.: 1.2644 g/l (0.0783 lb/ft^3)

6) Molar volume @ 1 atm.: (calculated)
$\bar{v}$ = 22,200 cc/mole @ 0°C
= 24,250 cc/mole @ 25°C
= 24,800 cc/mole @ 32°C
= 25,450 cc/mole @ 40°C
= 28,730 cc/mole @ 83°C

7) Critical Constants:
T_c = 9.7°C = 282.8°K
P_c = 50.5 atm.
d_c = 0.22 g/cc
$\bar{v}_c$ = 127.6 cc/mole
Z_c = 0.268

8) Latent Heats: Fusion; 28.547 cal/g (-169°C)
Vaporization; 115.39 cal/g (-103.7°C)

9) Heat of formation: ΔH_f° = 12,496 cal/mole @ 298°C

10) Heat of combustion: ΔH_c° = -337,230 cal/mole @ 298°C

11) Heat capaticy: (Ideal gas state)

$$c_P^* = 2.830 + (28.601\times10^{-3})T + (-8.726\times10^{-6})T^2$$

12) c_P/c_V = 1.18 @ 100°C
1.26 @ 15°C
1.35 @ -91°C

13) Viscosity: μ = 0.0093 centipoise @ 0°C
0.0101 centipoise @ 25°C
0.0106 centipoise @ 40°C
0.0115 centipoise @ 83°C
μ_c = 0.0215

14) Thermal Conductivity: k = 0.0101 BTU/(hr)(ft^2)(°F/ft) @ 32°F

15) Molar volume at normal boiling point: (calculated)

$$V_o = (r_o/1.18)^3 = 46.0$$

16) Collision diameter, $r_o = 4.232$ Å

17) Force constant, $\varepsilon/k = 205°K$

18) Calculated diffusivity in EDC from Wilke-Chang equation:

$$D_A = 3.51\times10^{-5} \text{ cm}^2/\text{sec} @ 32°C$$

(Balasubramanian et al.: 2.92×10^{-5} cm^2/sec @ 32°C)

19) Henry's Law constant for C_2H_4 in EDC:
(Balasubramanian et al.)

$$H_A = 3.27\times10^{4} \text{ atm(cc/mole)} @ 32°C, 1 \text{ atm.}$$

20) Solubility of C_2H_4 in EDC: (Seidell [28])

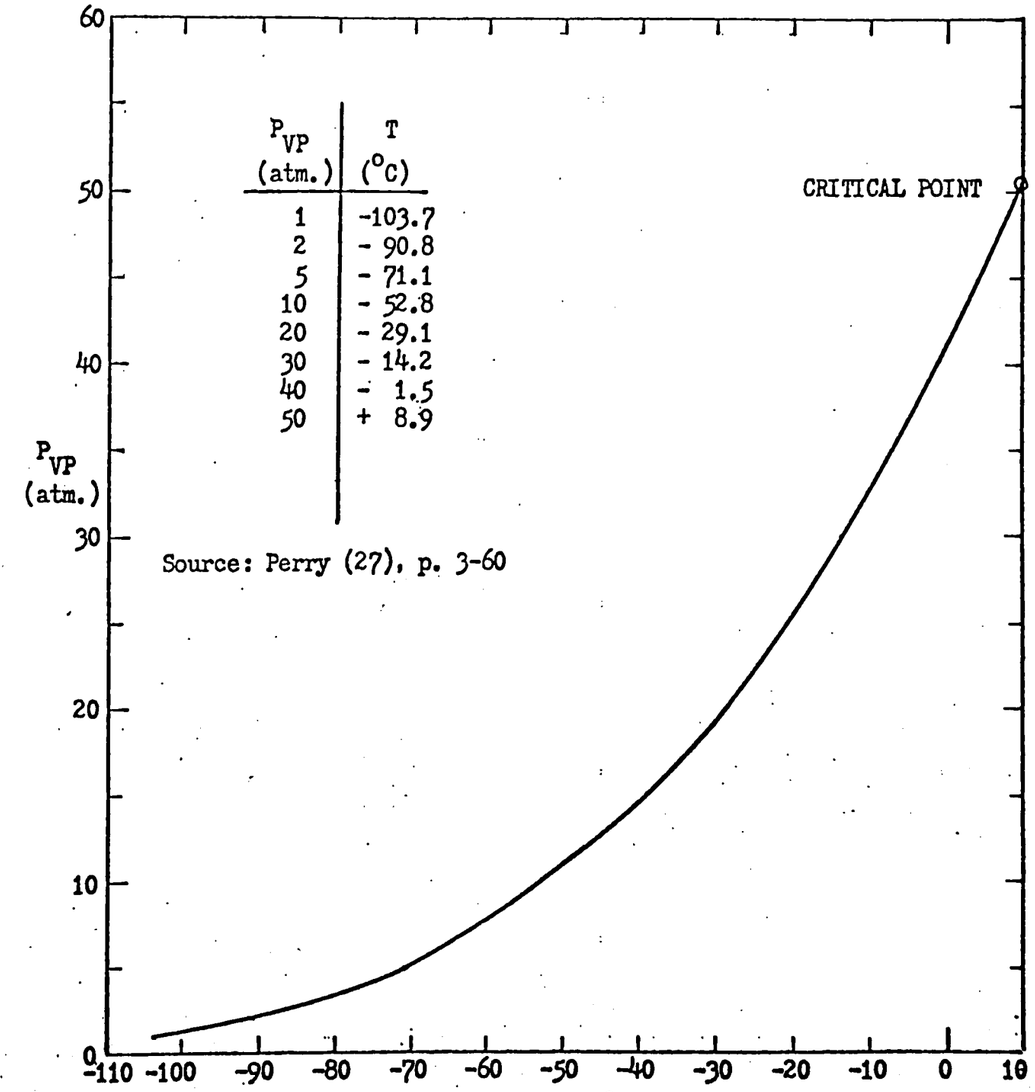
X = cc of ethylene (0°C, 760 mm) in 1 cc of EDC

P =	X =
50 mm Hg,	0.25
100	0.55
200	1.15
300	1.80
400	2.40
500	3.00
600	3.55
700	4.15
760	4.50

21) Pitzer Accentric Factor = 0.0 (T_s=-65°C, P_s=6.5 atm.)

Primary source of the above data is Perry [27].

FIG. C-1 VAPOR PRESSURE CURVE FOR ETHYLENE



P_{VP} (atm.)	T (°C)
1	-103.7
2	- 90.8
5	- 71.1
10	- 52.8
20	- 29.1
30	- 14.2
40	- 1.5
50	+ 8.9

Source: Perry (27), p. 3-60

APPENDIX D

PROPERTIES OF MISCELLANEOUS MATERIALS

1) 1,1,2-Trichloroethane (1,1,2-T). (36)

   (a) Chemical Formula: $C_2H_3Cl_3$

   (b) Formula Weight: 133.41

   (c) Vapor Pressure: (See Fig. D-1)

   (d) Melting Point: -36.7°C

   (e) Boiling Point: 133.9°C @ 1 atm.

   (f) Latent Heats: Fusion; 2700 cal/mole @ -36.7°C
   Vaporization; 8300 cal/mole @ 113.9°C
   9570 cal/mole @ 25°C

   (g) Density: d = 1.44 g/cc @ 25°C

   (h) Heat of Formation: ΔH_f° = -42,700 cal/mole (liquid)

2) Hydrogen Chloride (HCl). (38)

   (a) Solubility in Water: (760 mm) X = grams/100 g H_2O

T =	0°C,	X = 82.3
	30°C,	67.3
	40°C,	63.3
	50°C,	59.6
	60°C,	56.1

   (b) Heat of Solution: Approx. -30,000 BTU/lb-mole of HCl for concentrations below 0.1M.

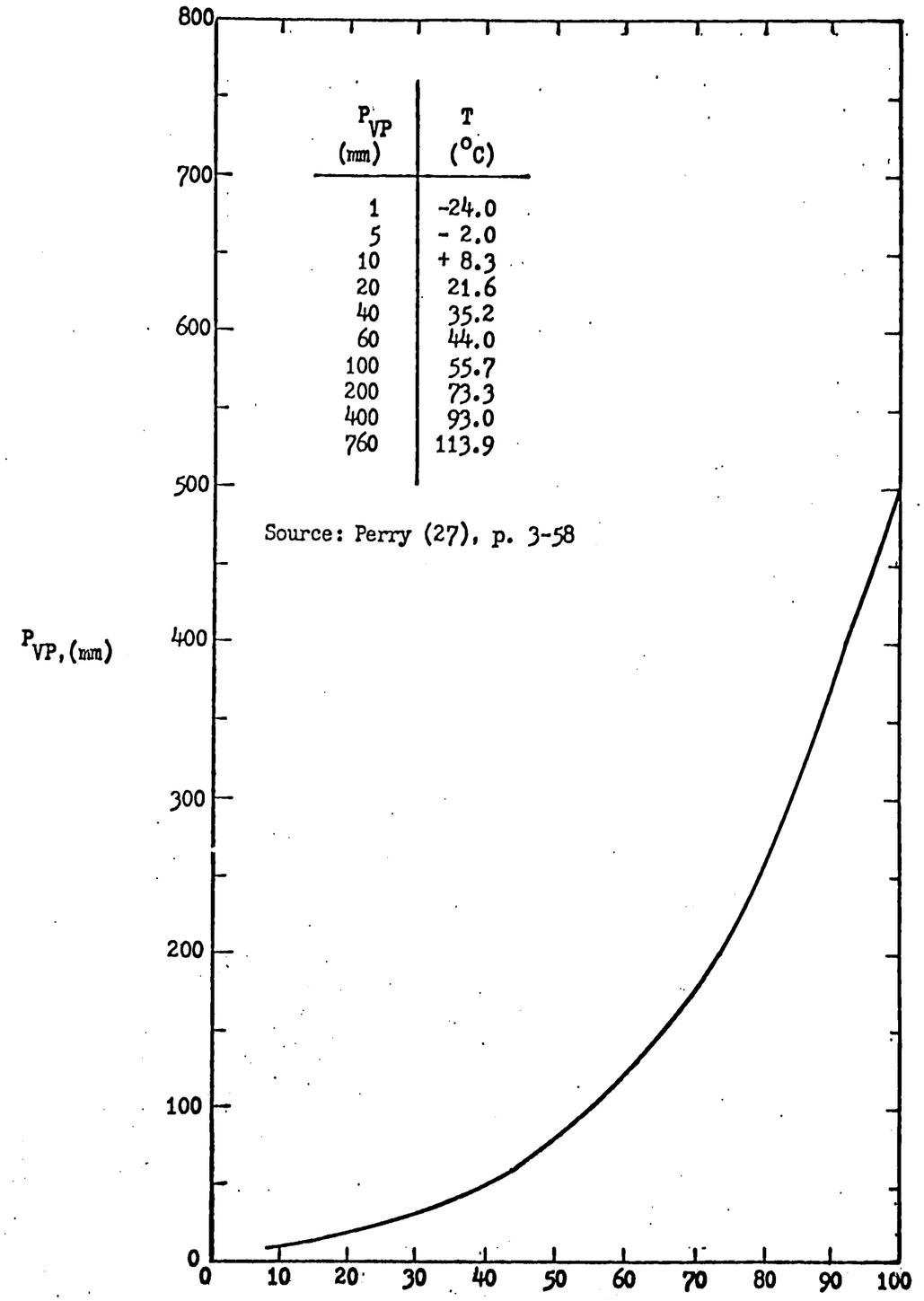
Primary source of data for 1,1,2-T: Stull et al., "The Chemical Thermodynamics of Organic Compounds," Wiley, New York (1969).

Primary source of data for HCl: Hougen, O. A. and K. M. Watson, "Chemical Process Principles," Wiley, New York (1943).

FIG. D-1 VAPOR PRESSURE CURVE FOR 1,1,2-TRICHLOROETHANE (1,1,2-T)

P_{VP} (mm)	T (^{o}C)
1	-24.0
5	- 2.0
10	+ 8.3
20	21.6
40	35.2
60	44.0
100	55.7
200	73.3
400	93.0
760	113.9

Source: Perry (27), p. 3-58



APPENDIX E

	Nomenclature	Units
C	Observed conversion of ethylene	mole %
C'	Acutal conversion of ethylene	mole %
C_C°	Molar concentration of chlorine in the bulk phase	moles/cc
C_C^*	Equilibrium concentration of chlorine at gas-liquid interface of chlorine bubble	moles/cc
F_E	Ethylene feed rate	gmoles/min
F_C	Chlorine feed rate	gmoles/min
F_E'	Unreacted ethylene going to bulk vapor phase from ethylene bubbles	gmoles/min
F_C'	Unreacted chlorine going to bulk vapor phase from chlorine bubbles	gmoles/min
F_C''	Rate of chlorine transfer from bulk liquid phase to bulk vapor phase	gmoles/min
F_H'	Rate of HCL transfer from bulk liquid phase to bulk vapor phase	gmoles/min
F_{ED}'	Rate of EDC vapor swept along with ethylene	gmoles/min
F_{ED}''	Rate of EDC vapor going to bulk vapor phase with chlorine	gmoles/min
F_{ED}'''	Rate of EDC vapor going from bulk liquid phase to bulk vapor phase	gmoles/min

F	Flow rate of exit gases from reactor	gmoles/min
F_2	Reflux flow rate	gmoles/min
F_1	Flow rate of exit gases from condenser	gmoles/min
P	Reactor pressure	atm.
P_E'	Ethylene vapor pressure in bulk vapor phase	atm.
P_C'	Chlorine vapor pressure in bulk vapor phase	atm.
P_H'	HCL vapor pressure in bulk vapor phase	atm.
P_{ED}'	EDC vapor pressure in bulk vapor phase	atm.
P_E''	Ethylene vapor pressure in condenser	atm.
P_C''	Chlorine vapor pressure in condenser	atm.
P_H''	HCL vapor pressure in condenser	atm.
P_{ED}''	EDC vapor pressure in condenser	atm.
T	Reactor temperature	^oC
T'	Reflux temperature	^oC
x_C'	Mole fraction of chlorine in reflux	

APPENDIX F

Bibliography

[1] Weisser, E. P., Chem. Eng. Progr., 1965, 61(4), p. 86.

[2] Danchwerts, P. V., "Gas-Liquid Reactions," McGraw-Hill, New York (1970).

[3] Calderbank, P. H., Trans. Instn. Chem. Engrs., 1958, 36, p. 443.

[4] Calderbank, P. H., Trans. Instn. Chem. Engrs., 1959, 37, p. 173.

[5] Calderbank, P. H. and Moo-Young, M. B., Chem. Engr. Sci., 1961, 16, p. 39.

[6] Calderbank, P. H., et. al., Proceedings of Third European Symposium on Chemical Reaction Engineering, Oxford, Pergammon Press, 1964, p. 91.

[7] Seaton, G. W., M.S. Thesis, Lehigh University, 1970.

[8] Balasubramanian, S. N., et. al., IEC Fund., 1966, 5(2), p. 184.

[9] Desai, N. R. and Viswanath, D. S., IEC Fund., 1972, 11(1), p. 26.

[10] Perry, R. H., et. al. (editors), "Chemical Engineers' Handbook," 4th Edition, McGraw-Hill, New York (1963).

[11] Cooper, C.O.O.M., Unpublished notes on possible theoretical models for autorefrigerated systems.

[12] Olah, G. A., et. al., "Friedel-Crafts and Related Reactions," John Wiley & Sons, Inc., 1964.

[13] Jack, H., "Physical Organic Chemistry," McGraw-Hill, New York, 1962.

[14] Gould, E. S., "Mechanisms and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1959.

[15] Dickinson, R. G. and Carrico, J. L., J. Am. Chem. Soc., 1934, 56, p. 1473.

[16] Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentic-Hall, Inc., New Jersey (1969).

[17] Norrish, R. G., J. Chem. Soc., 1926, 123, p. 3006.

[18] Farina, I. H., Chem. Eng. Sci., 1970, 25, p. 744.

[19] Galitzenstein, E. and Woolf, C., J. Soc. Chem. Ind., 1950, 69, p. 289.

[20] Heinz Heinemann, Chem. Tech., 1971 (May), 1, p. 286.

[21] Denbigh, K., "The Principles of Chemical Equilibrium," Cambridge, London (1968).

[22] Emmett, P. H., Sabatier, P. and Reid, E. E., "Catalysis - Then and Now," Franklin Publishing Co., Englewood, New Jersey (1965).